PB81-214900

Solid Waste: Methodology for Evaluation
Volume I: Tests for Potential Mobility of Toxic Components as Leachates

Battelle Columbus Labs., OH

Prepared for

Environmental Protection Agency
Washington, DC

Jan 81

U.S. Department of Commerce
National Technical Information Service
NTIS

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO.

2.

3. Recipient's Accession No. PB81 214900

4. Title and Subtitle
Solid Waste: Methodology for Evaluation Volume I Tests for Potential Mobility of Toxic Components as Leachates SW-196c.1

5. Report Date January, 1981

6.

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8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) 68-03-2552
(G)

12. Sponsoring Organization Name and Address
U.S. Environmental Protection Agency
Effluent Guidelines Division (WH-552)
Washington, D.C. 20460

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Battelle Columbus Laboratories conducted this research program to develop a method for assessing potential mobility of organic compounds from a waste codisposed in a municipal landfill. Inorganic constituents were monitored to provide a basis for comparison with previous research in the field using distilled water, 0.5 N acetic acid titration (EPA) extraction procedure-EP), and other leaching media. A literature survey and contacts with key scientists served as the basis for assessing state-of-the-art leachate research. A quality assurance study to assess the precision and accuracy of analytical methods to be used to evaluate the leachates and wastes was conducted prior to initiation of leachate research.

An interlaboratory comparison study of potential mobility procedure developed by Battelle and the total content method developed by Southern Research Institute (SoRI) was performed jointly by both laboratories. The ink pigment and still bottoms wastes were used for the interlaboratory comparison of the methods.

The advantages and disadvantages of the various analytical methods used throughout the program to determine metals and organics are discussed in detail. It was concluded that the leaching procedure and analytical methods used meet all of the original objectives of the program including feasibility of implementation at a cost of under $1850 per sample.

17. Document Analysis a. Descriptors

Gas Chromatography
Mass Spectrometry
Emission Spectroscopy
Solid Wastes
Extraction
Atomic Absorption

b. Identifiers/Open-Ended Terms

GC/MS
Inductively Coupled Plasma

c. COSATI Field/Group 07B, 07C

18. Availability Statement: Release unlimited

19. Security Class (This Report) Unclassified

20. Security Class (This Page) Unclassified

21. No. of Pages 135

22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

PB81-214900

Prepublication issue for EPA libraries
and State solid waste management agencies

SOLID WASTE:

METHODOLOGY FOR EVALUATION

Volume I
Tests for Potential Mobility of Toxic Components as Leachates

This report (SW-196c.1) was prepared under contract no. 68-03-2552
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U.S. ENVIRONMENTAL PROTECTION AGENCY
1981

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FOREWORD

On May 19, 1980 (45 FR 33122) the Environmental Protection Agency promulgated criteria for identifying wastes which pose a potential hazard to human health or the environment if improperly managed. These criteria were promulgated under the authority of Section 3001 of the Resource Conservation and Recovery Act (PL 94-580). During the development of these criteria, EPA needed to establish methodology to evaluate wastes relative to the aspects of potential mobility of toxic components (leaching) from the wastes and total content of toxic species in the waste. This report is divided into two volumes. Volume I is an evaluation of test methodology for the potential mobility of toxic components from wastes, and volume II is an evaluation of test methodology for the content of extractable toxic species present in wastes.

During the development of the regulations, EPA found that there was pervasive evidence that the contamination of groundwater through the leaching of waste contaminants from land disposed wastes is one of the most prevalent pathways by which toxic waste constituents migrate to the environment. EPA addressed this problem by developing a test procedure, called the Extraction Procedure, (40 CFR Part 261.24) to identify wastes from which hazardous concentrations of particular toxic constituents are likely to leach into the groundwater under conditions of improper management. The particular condition of improper management modelled by this procedure is codisposal of toxic wastes in an actively decomposing municipal landfill. EPA realized in making its codisposal assumption that actively decomposing municipal waste landfills generate more aggressive leachate media than other landfills.

EPA conducted a number of studies to develop the Extraction Procedure. These studies were aimed at developing a leaching medium that would model the leachate generated by actively decomposing refuse, yet have a low inherent biological toxicity. Low toxicity was necessary so that bioassay procedures could be employed to measure the presence of significant concentrations of toxic species in the resulting extract. The Agency found that it could not incorporate all the desired properties into the extraction media given the Congressional and Court-mandated deadlines. Thus, only the acidic nature of municipal landfill leachate was incorporated into the Extraction Procedure promulgated on May 19, 1980.

Volume I of this report describes one of several studies being conducted by the Agency to evaluate and improve leachate test methodology to be applied to wastes in an actively decomposing municipal landfill. Much emphasis in this work was placed on studying the leachability of organic components of wastes.

As part of an overall study to characterize wastes, EPA is evaluating analytical methods for both leachable components and total content of wastes. Volume II of this report presents part of the work performed to date in this area.

ABSTRACT

Battelle's Columbus Laboratories conducted this research program to develop a method for assessing potential mobility of organic compounds from a waste codisposed in a municipal landfill. Inorganic constituents were monitored to provide a basis for comparison with previous research in the field using distilled water, 0.5 N acetic acid titration (EPA extraction procedure-EP), and other leaching media. A literature survey and contacts with key scientists served as the basis for assessing state-of-the-art leachate research. A quality assurance study to assess the precision and accuracy of analytical methods to be used to evaluate the leachates and wastes was conducted prior to initiation of leachate research.

From a total of 23 wastes collected for the program, 6 samples were selected for evaluation. Initial assessment of the effect of the mixing device design and the effect of leaching media upon leachability of organic and inorganic constituents was accomplished using a dewatered (25 percent solid) public owned treatment works (POTW) sludge. The EP was used to evaluate a stirring-type mixing device (made by ADMCo) and a tumbling-type mixing device (designed by NBS for EPA). The NBS tumbler was selected for all subsequent studies on the basis of (1) superior leaching ability for volatile organics, (2) comparable leaching ability for metals and semivolatile organics, (3) ease of operation, and (4) ability to handle a wider range of sample types. Seven of the 17 leaching media were selected for additional studies on the basis of the results of this initial task. These media were distilled water, acetic acid (EP), 0.1 M acetate buffer (pH 4), two pH 5 sodium citrate buffers (0.02 M and 0.05 M), and 0.01 M sodium citrate (pH 5). Five wastes were leached with each of these seven media. The five wastes were a baghouse dust, an unidentified organic still bottom, an ink pigment waste, a pharmaceutical waste, and a coal gasification tar. The observed effect of leaching medium composition on organic mobility was slight, whereas the effect on metal mobility was frequently very large and concentration dependent. Comparable results were obtained with the EP and 0.1 M acetate buffer while the addition of citrate generally increased mobility of metals dramatically. There was no significant difference in mobility of metals or organics by adding hydrosulfite or surfactant, respectively.

Quality assurance measures adopted for the program included spikes, three or five replicates, blanks and appropriate calibration/performance standards. Descriptive statistics, including mean recoveries, standard deviation and relative standard deviations were augmented by comparisons of secondary characteristics to evaluate the leaching results.

An interlaboratory comparison study of the potential mobility procedure developed by Battelle and the total content method developed by Southern

Research Institute (SoRI) was performed jointly by both laboratories. The ink pigment and still bottoms wastes were used for the interlaboratory comparison of the methods. The data for metal analyses were comparable using atomic absorption spectrophotometry or inductively coupled argon plasma. The comparison of volatile organic analyses was excellent especially when one considers that Battelle used a carbon disulfide extraction method with analysis by gas chromatography and SoRI used purge and trap EPA Method 624 that involves analysis by combined gas chromatography-mass spectrometry. Data for semivolatile organic constituents obtained by both laboratories using EPA Method 625 were also comparable.

The advantages and disadvantages of the various analytical methods used throughout the program to determine metals and organics are discussed in detail. It was concluded that the leaching procedure and analytical methods used meet all of the original objectives of the program including feasibility of implementation at a cost of under $1850 per sample.

The solid waste leaching procedure developed on this program when used with distilled water as the leaching medium is recommended for the preparation of a leachate that can be used to assess the potential mobility of organic components from solid wastes codisposed with municipal wastes in a landfill except when the waste contains significant amounts of immiscible and nondispersible oils. The carbon disulfide extraction procedure with analysis by glass capillary column gas chromatography as used on this program is recommended as an optional procedure for the determination of volatile organics in solid wastes and solid waste leachates. The modified Method 625 used for this program, involving a single extraction under acidic conditions and the determination of both neutral and acidic semivolatile components in a single GC-MS run using a glass capillary column, is recommended as an optional procedure for the determination of semivolatile organics in solid wastes and solid waste leachates.

We recommend that future research programs be undertaken to:

- Develop protocols and procedures for dealing with oily wastes

- Develop a relatively simple solid waste extraction method that will give good recoveries of low levels of the polar and acidic semivolatile organics as well as the less polar neutral components, and

- Conduct an interlaboratory validation study of the leaching procedure, leachate analysis methods, and total content analysis methods, involving a number of wastes selected to represent waste types and six or more laboratories.

This report was submitted in fulfillment of Contract No. 68-03-2552 by Battelle's Columbus Laboratories under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1 to August 29, 1980.

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ACKNOWLEDGMENTS

The assistance and technical support provided by the Task Officers for this program, Mr. Mike Carter and Dr. Dean Neptune of the Effluent Guidelines Division, is appreciated by Battelle. We are indebted to Mr. David Friedman and Dr. Jim Poppiti of the Office of Solid Waste who provided valuable technical direction.

The cooperation and technical guidance of Dr. Gene Meier, EMSL-Las Vegas, which significantly enhanced the quality of this research program is gratefully acknowledged.

The Battelle researchers appreciated this opportunity to interact and collaborate with Chip Miller, Ruby James and Walt Dixon of Southern Research Institute who conducted the total content research effort. The staff of the Center for Analytical Chemistry, National Bureau of Standards, is acknowledged for providing the NBS tumbler extractors and for helpful technical discussions.

Mr. Ray Smithson and Mr. Ron Clark of Battelle provided management assistance that was invaluable to the project. Ms. Linda Delma's professional contributions in production and organization of weekly reports and coordination of program activities are appreciated by program participants.

SECTION I

INTRODUCTION

The EPA's Office of Solid Wastes (OSW) of the Office of Water and Waste Management is required by the Resource Conservation and Recovery Act of 1976 (RCRA) to identify wastes that may be hazardous and to select those wastes which require special management. The EPA specifies an extraction procedure (EP) involving the use of acetic acid to assess the leachability of certain toxic organic compounds and chemical elements from wastes for use in determining whether a waste is a hazardous waste under RCRA(1). The research effort by Battelle's Columbus Laboratories described here, entitled, "Development of Methodology for the Evaluation of Solid Wastes", was established by the OSW and the Effluent Guidelines Division (EGD) of EPA to continue development of the potential mobility procedure and to evaluate methods for the total content of toxic compounds in waste materials covered by the RCRA legislation. Major emphasis was placed on potential mobility of organic compounds; metal analyses were also conducted so that additional valuable comparisons with EP results could be realized.

Several criteria were designated by EPA for development of a leaching procedure. The method developed had to be:

- Technically sound
- Feasible and practical to implement
- Designed to simulate the leachability expected to occur in municipal landfill environments
- Within the capabilities of a production-type laboratory
- Cost no more than $1,850 per sample analysis when performed routinely.

The municipal landfill environment was targeted since the mode of disposal of interest to OSW is codisposal of a given waste in a municipal landfill.

Battelle performed two tasks prior to initiation of leaching research. First, a state-of-the art literature search was conducted. Because Battelle researchers were familiar with the analytical approaches for leaching method development, an exhaustive literature search was unnecessary. Key publications and information were assembled by referring to latest editions of EPA reports and methods and searching recent selected technical journals. Personal contacts, including scientists currently active in this area of research, EPA researchers, and appropriate ASTM members presently associated with development of leaching methods, were relied upon to supplement printed information.

Second, based on this survey, several analytical techniques were identified that would be required for the research program. Since a variety of factors would be examined throughout the course of the study, the inherent analytical method variabilities were established prior to use by performing an exhaustive analytical method precision study. A detailed description of this study is presented in the Quality Assurance section of this report for:

- Atomic Absorption Spectrophotometry (AAS)
- Inductively Coupled Argon Plasma Spectrometry (ICAP)
- Gas Chromatography (GC)
- Gas Chromatography-Mass Spectrometry (GC-MS),

as applied to the analysis of the leachates from dewatered sludge from a Public Owned Treatment Works (POTW).

The research program that was designed included six subtasks to be conducted concurrently when possible. These subtasks were:

Task 1. Procurement of Waste Samples
Task 2. Physical Compatibility of Wastes
Task 3. Comparison of Extractor Precision
Task 4. Effect of Leaching Media on Waste
Task 5. Effect of Waste on Leachate Composition
Task 6. Interlaboratory Comparison Study.

The scope of each task, to be described in detail in this report, will be summarized here.

TASK 1. PROCUREMENT OF WASTE SAMPLES

The requirement that the leaching procedure developed must be applicable for a broad range of wastes made it mandatory that a spectrum of wastes that are difficult to handle be obtained for examination. The most complex samples were sought so that the worst case waste could be included in the method development phase. The criteria used to select waste samples included:

- High percent solid content
- High total organic content
- Large number of organic compounds present at high concentration
- High total inorganic content
- Wide pH range.

The wastes selected for study included one or more meeting each criterion and, preferably, wastes meeting more than one of these criteria. A special attempt was made to obtain wastes representative of anticipated industrial problem wastes.

TASK 2. PHYSICAL COMPATIBILITY OF WASTES

The research performed for developing a leaching method required the evaluation of a variety of leaching media applied to numerous solid wastes. This evaluation could be accomplished only if the wastes studied were compatible throughout the conduct of the method. Thus, each waste obtained from the sources identified was evaluated according to the ability and ease of:

- Separation by centrifugation
- Separation by filtration, and
- Dispersion in extraction device.

Based upon these observations, eight wastes were selected for further study which would challenge the centrifugation, filtration, and extraction steps.

TASK 3. COMPARISON OF EXTRACTION PRECISION

Two extraction devices were considered for the program based upon the literature search:

(1) Stirrer Extractor-Associated Design and Manufacturing Company (ADMCo)

(2) Tumbler extractor developed for EPA by the National Bureau of Standards (NBS).

These two devices were used to extract the dewatered POTW sludge using EPA's extraction procedure (EP). Any differences in the precision of the data obtained or losses of analytes of interest that might be attributed to the extraction equipment were identified in this manner.

TASK 4. EFFECT OF LEACHING MEDIA ON WASTE

Based upon the survey of scientists and published literature, Battelle researchers selected seventeen candidate leaching media which met one or all of the following criteria:

- Likely to be present in or simulate components present in a municipal landfill
- Nontoxic for bioassay
- Minimum analytical interference potential for organic and inorganic analysis.

The dewatered POTW sludge was leached with each of these media and analyzed for organic and inorganic priority pollutant compounds to assess efficiency and applicability of each medium.

TASK 5. EFFECT OF WASTE ON LEACHATE COMPOSITION

The results from Task 4 and supplementary information regarding the chemical nature of each medium were evaluated to select a small number of media for study with a variety of solid wastes. In this manner, it was possible to determine if the type of waste affected the relative analytical results obtained by using the leaching procedure with a variety of media.

TASK 6. INTERLABORATORY COMPARISON

Two research organizations participated in this study. Battelle's Columbus Laboratories (BCL) developed the potential mobility or leaching procedure, and Southern Research Institute (SoRI) developed the total content method. The final task of this program required the participation of both laboratories. Samples and analytical methods were exchanged and both organizations performed the leachate procedure and analysis for total content in order to obtain comparative data.

The research program discussed in detail in this report was completed in only 6 months due to the urgency of the EPA's need for defensible analytical methodology in this important area. Therefore, the Conclusions and Recommendations sections of this report include several suggestions for future research. Battelle recommends that extensive interlaboratory validation studies be conducted for both the potential mobility and total content methods.

SECTION II

CONCLUSIONS

The types of waste covered by the Resource Conservation and Recovery Act vary considerably in respect to composition and physical properties. The wastes selected for the program included a variety of wastes high in solids content and containing significant amounts of organic and inorganic pollutants.

The leaching media studied included dilute acetic acid as used in the EPA Extraction Procedure (EP), distilled water, and 15 additional media selected to provide variable conditions that might occur in a municipal landfill. The distilled water leachate was as effective as the other media in leaching organic components and does not interfere with either bioassay or analytical procedures.

The results obtained using 0.1M sodium acetate buffer, pH 4.0, were similar to the results obtained using the EP for the leaching of metals. The EP using a tumbler-type extractor was found to be a reproducible means of generating leachates from many types of wastes. The stirrer extractor was shown to be inadequate since significant losses of volatile organic compounds were observed. Citrate buffer was often more aggressive than acetate buffer for the leaching of metals. The aggressiveness of buffered acidic and reducing media toward leaching of metals was highly metal and sample dependent.

The results of the interlaboratory comparison study conducted jointly by Battelle and Southern Research Institute indicate that the solid waste leaching procedure developed for this study is reproducible. The procedure is easy to use and is suitable for many types of wastes and analytes. However, the procedure does not provide for obtaining a representative aliquot of a two-phase liquid leachate that would result from leaching an oily waste. Although the leaching media studied were selected to mimic conditions occurring in a municipal landfill, the degree to which this procedure reproduces the leaching of organics in a codisposal environment is unknown at this time.

SECTION III

RECOMMENDATIONS

The solid waste leaching procedure developed on this program is recommended for the preparation of a leachate that can be used to assess the potential mobility of chemical components from a solid waste placed in a landfill. More specifically it is recommended that the procedure be used with distilled water as the leaching medium for generation of a leachate which can be analyzed to assess the potential mobility of organic components from a solid waste codisposed with municipal wastes in a landfill.

The procedure can be used to prepare leachates of various different types of wastes to compare the potential mobilities of organic components from those wastes. It should be recognized, however, that the composition of leachates produced from a waste in the field can be affected very significantly by uncontrolled factors such as amount of rainfall, evaporation rates, water flow rates and water flow profiles at a landfill site. Consequently, the composition of an actual leachate produced from a waste in the field should not be expected to be the same as a leachate generated in the laboratory under controlled conditions.

It should also be recognized that although the leachability of organic components was not significantly affected by the leaching medium composition, the leachability of inorganic components was very drastically affected by leaching medium composition. Therefore, if it is desired to determine the site specific leachability of inorganic components, it is recommended that the leaching medium be carefully selected based on the composition of the waste, the composition and relative amount of material codisposed with the waste, the composition of the soil mixed with the waste, the chemical and biological reactions that can be expected in the particular landfill situation, and the water flow profiles that can be expected.

One aspect of the solid waste leaching procedure that was not studied in this program is the potential removal of soluble organic components by adsorption by the membrane filter used in the filtration step. It is very possible that the relatively lipophilic cellulose ester filter used will remove significant amounts of soluble components, especially the less polar components. However, if the filtration step is omitted, relatively high concentrations of organic compounds may remain in the leachate as part of the particulate matter that is not removed by centrifugation. It is therefore recommended that the adsorption of low levels of soluble organics by cellulose ester membrane filters and the use of less lipophilic final filters, e.g. glass fiber or regenerated cellulose filters, be studied in a future research program.

For reasons discussed elsewhere, the solid waste leaching procedure developed in this program is not suitable for use with wastes that contain significant amounts of immiscible and nondispersable oils. Since such oily wastes are relatively common, it is recommended that future efforts include the development of protocols and procedures for dealing with oily wastes. This effort should be combined with the membrane filter study because immiscible oils or solvents can be very detrimental to cellulose ester filters.

The analytical procedures used on this program for the determination of volatile and semivolatile organics often deviated considerably from EPA Methods 624 and 625 in order to achieve improvements in cost effectiveness. However, the quality of the data obtained, in terms of both precision and accuracy (percent recovery) was not sacrificed. Consequently, it is recommended that the CS_2 extraction method with GC-FID analysis for volatile organics be accepted as an optional method for both leachate analyses and total content analyses for solid waste studies whenever possible. It is recognized that in some cases the presence of large amounts of interferences may preclude the use of any method other than a GC-MS procedure.

It is also recommended that the modified methylene chloride extraction procedure, employing a single extraction under acidic conditions and a single GC-MS run using a glass capillary column, be accepted as an optional procedure for the analysis of semivolatile organic priority pollutants in leachates in all cases except when benzidine is of specific interest. It should be recognized, however, that Method 625 is not reliable for the determination of low levels of benzidine unless special modifications are made to prevent the oxidative degradation of benzidine.

For the extraction of semivolatile organics from solid wastes for total content analyses, it is recommended that a single neutral/acid fraction for analysis by glass capillary column GC-MS be accepted as an optional procedure. Furthermore, it is recommended that the homogenization-extraction be performed without the addition of water and in the presence of a drying agent to enhance the recoveries of polar components. This step could be coupled with Soxhlet extraction to achieve an exhaustive extraction, if desired. Finally, it is recommended that cleanup steps in addition to GPC be studied in an effort to prevent the precipitation during the concentration step of material that might adsorb and thus remove components of interest.

SECTION IV

LITERATURE REVIEW

Prior to initiating laboratory investigations, a literature search was conducted to examine the current state-of-the-art in leaching methods. Because this study was primarily concerned with the potential mobility of organic constitutents of wastes, particular attention was paid to previous research dealing with leaching of organic compounds. The search provided pertinent information about the characteristics of the leaching media that have been used, the leaching test conditions that have been specified, and the extent to which precise control of these conditions has been maintained. Finally, the search examined which leaching test conditions have been previously studied and what results have been obtained.

Because Battelle researchers were familiar with leaching methods and the associated analytical techniques, an exhaustive search of the literature on leachates was unnecessary. Due to this previous experience, attention was focused on the latest developments in the leaching field. The resources used during the literature search included

- Computerized retrieval of published abstracts using key word searching of the Chemical Abstracts Envirolines, National Technical Information Service, and Pollution Abstracts data files.

- Active searching of most recent government publications and professional journals for articles too current for inclusion in the files of abstracting services.

- Personal contact with scientists currently active in the fields of leaching medium selection, leaching methology development, and leachate characterization. The individuals contacted included government and academic researchers and ASTM members presently devoted to leaching method studies.

The literature search reinforced the belief that the majority of investigations into leachability of constituents from solid wastes have been confined to studying the inorganic constituents. Earlier studies that did include an assessment of the mobility of organic constituents usually presented data for organic compounds as "Total Organic Content" or as other general classes of compounds, such as tannins and lignins(2,3). Only more recently have researchers attempted to analyze for specific organic constituents.

Robertson, et al., investigated various organic compounds that were being leached from a sanitary landfill(4); Burrows and Rowe studied the ether-soluble constituents in landfill leachates(5); and Jones, et al., examined halogenated organic compounds leached from wastes(6).

The chemical and physical nature of leachates has been studied extensively, and comprehensive reviews have been published(7,8). Ideally, the leaching medium and test conditions used in a leaching test should reproduce the actual leachate and conditions to be encountered at the field disposal site, because the chemical composition of a leaching medium is highly site specific. The leachate percolating through a particular waste reflects the composition of all the materials through which that leachate has travelled and depends on such site characteristics as annual rainfall volume and composition, evapotranspiration, biological activity, and the nature of the surrounding soil and wastes(8).

Because of the diversity of the site conditions that are encountered in the field, no single leaching medium can accurately reproduce the composition of the actual leachate to be found in all situations. However, the factors that influence leaching medium composition have been identified (Table 1), and the relative influence of leaching activity can be estimated. The predominant factors inherent to leaching medium composition that directly relate to leaching ability are the proton and electron environments(9-11) and the presence of solubilizing agents(12,13).

The proton and electron environments have been determined for natural environments(14) and landfill leachates(7,15,16) by measuring the pH, redox potential, ionic strength, and buffering capacity. Lowenbach has evaluated the extent to which various leaching media have incorporated these factors(10).

Solubilizing agents include constituents such as complexing agents (hydroxyl ion, ammonia, EDTA), colloidal constituents (micelles or surfactants), and organic constituents (melanic materials, humic acids). These agents have a profound effect upon the mobility of inorganic and organic constituents of the waste, even when the agents are present at low concentrations. Most analyses of field leachates have failed to examine the possible presence of such agents, although some of the more recently developed leaching media have incorporated solubilizing agents(17,18).

The analytical techniques used in the leaching procedures(19-21) have been studied extensively(22-30), and the instrumental methods for use in analyzing the wastes and leachates have been investigated by several researchers(31-38). The report of Lowenbach provides a detailed summary of the procedures for over 30 available or proposed leaching methods(10). These leaching methods were evaluated with regard to the critical variables given in Table 1. A summary of the leaching variables for these proposed methods is presented in Table 2(9,39).

The studies of Ham and associates provide a comprehensive evaluation of the effects produced by systematically varying each of the leaching conditions given in Table 1(8,9,17,18,40,41). The studies of Lowenbach and Ham

TABLE 1. CRITICAL VARIABLES IN A LEACHING METHOD

I. Leaching Medium Composition
  - A. Proton and Electron Environment
    - 1) pH
    - 2) Redox potential ($p\epsilon$ or Eh)
    - 3) Ionic strength
    - 4) Buffering capacity
  - B. Presence of Solubilizing Agents
    - 1) Chelating agents
    - 2) Complexing agents
    - 3) Colloidal constituents
    - 4) Organic constituents

II. Leaching Conditions
  - A. Contact Area/Particle Size
  - B. Method of Mixing
  - C. Mixing Time
  - D. Temperature Control
  - E. Number of Leachings on the Same Solid
  - F. Number of Leachings with the Same Liquid
  - G. Solid to Liquid Ratio

TABLE 2. FREQUENCY OF TEST VARIABLE SPECIFICATIONS IN PUBLISHED LEACHING PROCEDURES

Critical Leaching Variable	Number of Published Leaching Procedures Specifying the Test Variable(a)
I. LEACHING MEDIUM COMPOSITION	
H_2O (distilled, deionized, distilled-deionized, or unspecified)	17
H_2O with pH adjustment or simple acid base	5
Site specific	1
Acetate buffer	1
Synthetic municipal landfill leachate	1
Synthetic natural rainwater	1
Bacterial nutrient media	1
Tests with more than one leachate	5
II. LEACHING CONDITIONS	
A. Contact Area/Particle Size	
10 Mesh	1
45-60 Mesh	2
100-200 Mesh	1
Unspecified	28
B. Temperature	
20°C "If Required"	1
95°C	2
Unspecified or Room Temperature	29
C. Method Mixing	
Mechanical Shaker	12
Mechanical Stirrer	8
Stir and Settle	3
Gas Agitator	3
Special Apparatus	4
No Mixing	2

TABLE 2. (CONTINUED)

Critical Leaching Variable	Number of Published Leaching Procedures Specifying the Test Variable[(a)]
D. Time of Mixing	
<1 Hour	5
1-24 Hours	7
24 Hours	11
48 Hours	3
72 Hours	2
>72 Hours	2
To Equilibrium	2
E. Number of Leachings on Same Solid	
1	24
3	1
5	1
7	1
10	2
Several	3
F. Number of Leachings with Same Medium	
1	31
>1	1
G. Solid to Liquid Ratio	
1:<4	5
1:4	5
1:5	3
1:6	2
1:7	1
1:9	1
1:10	4
1:>10	6
Varied	2
Calculated	3

(a) A total of 32 published leaching procedures were compared.

and associates were relied upon very heavily by researchers at Battelle in assessing what leaching media had been developed and what conditions had been recommended.

Once the search for leaching media and leaching conditions had been completed, the results from these past studies were critically evaluated. This evaluation was used to select the leaching media for use in the appropriate subtasks of this overall research program and the analytical techniques for use with the leaching method.

SECTION V

EXPERIMENTAL

SAMPLE COLLECTION AND SELECTION

Samples of sludges and other industrial wastes were collected at the initiation of the project from a variety of industries with emphasis given to samples known to contain high levels of solvent-extractable organic components or expected to cause problems during leachate generation or analysis. It was believed that the most complex samples available should be used for method development so that any method developed would be applicable to all sample types. The samples obtained are listed in Table 3. These samples include oily wastes, aqueous sludges, inorganic solids and organic solids. Some of the wastes had dense solids separated from the liquid phase, some contained no liquid phase, and one was gelatinous.

Some samples were collected specifically for this project at the waste generation site. These samples were preserved at 4°C prior to leachate generation. Two exceptions are the baghouse dust and fly ash samples which were not refrigerated. Many of the samples were provided by a commercial hazardous waste disposal facility and were received in five gallon plastic pails. Since these wastes had been exposed to ambient temperature for several months or more, no refrigeration was deemed necessary.

The pH and percent solids content were determined for all wastes received. For samples containing sufficient liquid, the pH was determined on the liquid phase. For solid samples or for those containing only small amounts of liquid, equal weights of sample and distilled water were mixed in a slurry and the pH was determined on the mixture after five minutes. All pH measurements were taken using an Orion Model 501 pH meter with a combination pH electrode. In some cases, oil in the waste caused difficulties in obtaining an accurate pH measurement.

For the determination of percent solids in the waste, a 100-g portion of the well-mixed waste was dried at 105°C overnight. The sample was weighed after cooling and the percent solids calculated from the remaining solid.

Many of the samples as received were inhomogeneous. In order to ensure that all replicate determinations performed would test the precision of the method and not the homogeneity of the waste, the wastes were thoroughly mixed prior to collection of an aliquot for leaching experiments. The method of mixing varied depending on the waste type. In some cases, a Teflon^{R}-coated spatula was used to stir the waste as thoroughly as possible. A motor-driven, Teflon^{R}-coated stirrer was used when feasible. Still, because of

TABLE 3. DESCRIPTION OF WASTE SAMPLES RECEIVED FOR THE STUDY

Description	pH	Percent Solids Content	Category[a]
POTW Raw Sludge	6.5	0.8	AS
POTW Dewatered, Chemically-treated Sludge	9.7	25.2	IS
Electroplating Sludge	9.0	15.2	AS
Latex Paint Sludge	7.8	14.9	AS
Lime Slurry Treatment Sludge	7.2	2.0	AS
Food Processing Sludge	5.6	0.5	AS
Coke Plant Sludge	9.0	3.1	AS
Still Bottom, Organic	3.6	35.9	OS
Fly Ash	10.9	100	IS
Baghouse Dust	6.3	99.3	IS
Pulp and Paper Sludge	6.5	28.9	OS
Coal Gasification Coal Tar Waste	6.8	49.7	OS
Oil Refining Oil Waste	3.6	81.6	OW
Machine Operation Waste	6.8	22.7	OW
Ink Pigment Waste	11.3	14.8	AS
Steel Mill Spent Acid	1.3	13.7	AS
Alkaline Cleaning Waste	11.4	2.6	AS
Engine Manufacturing Waste - Oils and Coolants	6.8	2.1	AS
Water Treatment Waste Acid Sludge	5.9	9.7	AS
Herbicide Manufacturing Acetone - Water Waste	7.5	17.4	AS
Herbicide Manufacturing Acid Waste	0.6	40.5	AS
Paint Manufacturing Waste	6.8	0.7	AS
Pharmaceutical Waste	6.5	19.0	AS

(a) AS = Aqueous sludge (>80% H_2O); OW = oily waste (>20% oil); IS = inorganic solid (>20% inorganic); OS = organic solid (>20% organic).

the nature of the wastes, thorough mixing was not always possible, and inhomogeneity of the waste cannot be excluded from contributing significantly to the overall precision obtained with the method.

Physical Compatibility

Each of the 23 wastes considered for use in this method development program was visually evaluated and categorized. A physical description for each waste was given according to consistency, color, and solid content. The definition of categories used to classify the samples is as follows:

Aqueous Sludge (AS) - Greater than 80 percent water
Oily Waste (OW) - Greater than 20 percent oil
Inorganic Solid (IS) - Greater than 20 percent inorganic content
Organic Solid (OS) - Greater than 20 percent organic content.

The processing techniques to be used or examined for use during the conduct of the leachate procedure included:

- Centrifugation
- Filtration
- Stirring
- Tumbling.

If a given processing technique could obviously not be used without damage to laboratory equipment, only a visual inspection was recorded.

The amenability of each waste to tumbling in the NBS extractor was considered to be the most critical evaluation of physical compatibility. For this investigation, 1500 ml of water was added to 75 gm of wastes contained in a glass bottle. Adequate dispersion of the waste in the leaching sequence was examined only for the most complex samples.

Leachate Generation

Two different sample extraction devices were used in this study for the generation of leachates. One device is a stirrer-based unit manufactured by Associated Design and Manufacturing Company, (ADMCo) Model No. 3736-M, consisting of a 2-liter stainless steel beaker and a motor-driven two-blade impeller.(1) The interior of the beaker and the impeller blades were Teflon^{R} coated per Battelle's special request to prevent metal contamination from the stainless steel. The tumbler system shown in Figure 1 is capable of tumbling four containers in an end-over-end fashion. This extracter was designed and provided by the National Bureau of Standards. Similar units are now commercially available (Associated Design and Manufacturing, Model No. 3740-4-BRE).

For the generation of leachate using the ADMCo stirrer, the conventional EPA extraction procedure was used.(1) The dewatered POTW sludge was the only sample extracted using this device. Since the sample was essentially a wet solid, no filtration prior to sample extraction was conducted. A 100-g portion of the well-mixed sample was placed in the 2-liter stainless steel

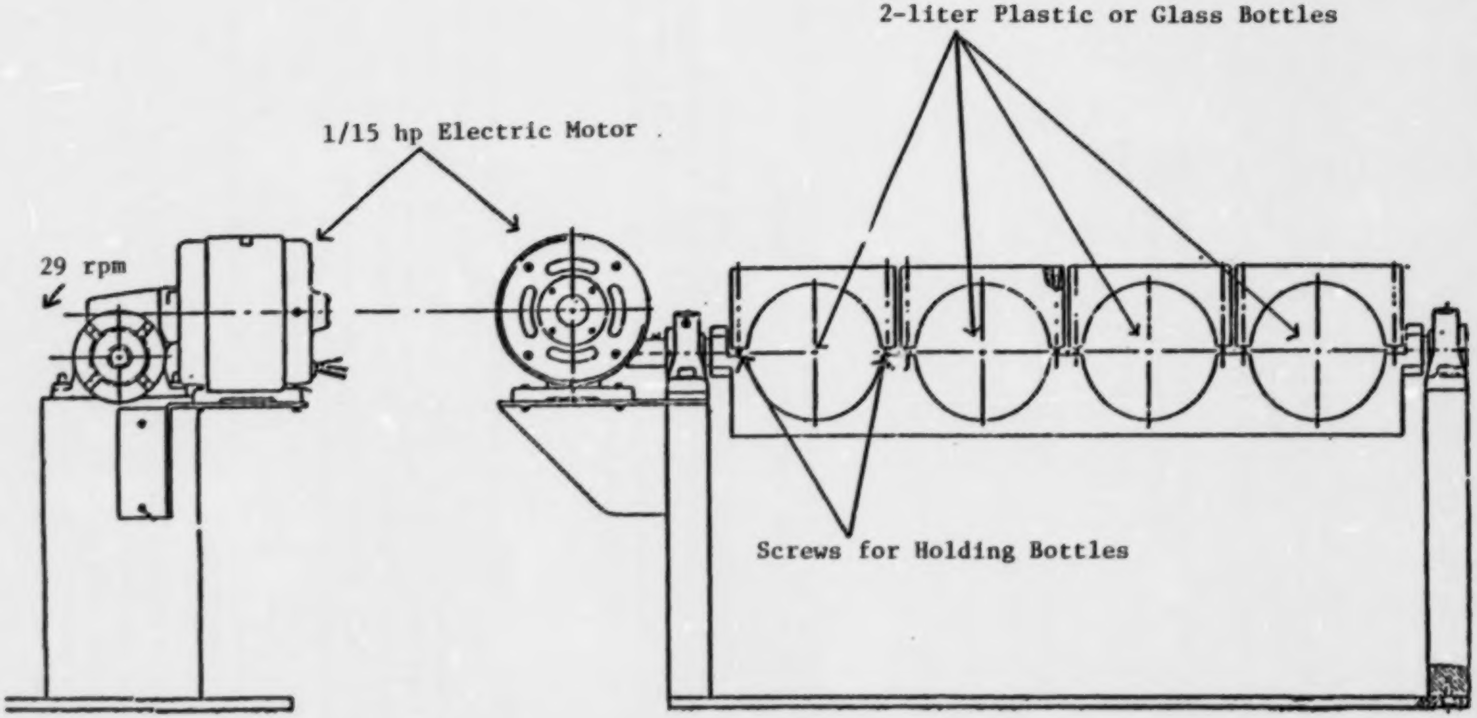

2-liter Plastic or Glass Bottles
1/15 hp Electric Motor
29 rpm
Screws for Holding Bottles

FIGURE 1. NBS-DESIGN ROTARY EXTRACTOR

beaker and 1600 ml of deionized water was added. The sample was stirred briefly and the pH was determined. If the pH was greater than 5.0, a portion of 0.5 N acetic acid was added and the sample was again stirred. The pH was measured and additional acetic acid was added until the pH was 5.0 ± 0.2 or until 400 ml of 0.5 N acid was added. The sample was stirred for 24 hours and the pH was checked periodically. Additional acetic acid solution was added to maintain pH 5.0 unless the maximum of 400 ml had been reached. If the pH of the solution was not less than 5.2 and the maximum amount of acid had not been added at the end of the 24-hour extraction period, the pH was adjusted to 5.0 ± 0.2 and the extraction was continued for an additional four hours with pH adjustments at each one hour interval. A blank, consisting of 1600 ml of deionized water plus the average amount of acetic acid used in the samples, was carried through the procedure. In four of the five replicate determinations on the dewatered POTW sludge, the maximum amount of acetic acid (400 ml) was added. The final pH of the leachate was greater than 7. However, the fifth replicate required only 150 ml of acetic acid to remain at pH 5.0 ± 0.2. Although the sample was mixed as thoroughly as possible prior to obtaining aliquots, sample inhomogeneity is suspected to be the cause of this variation.

Upon completion of the 14-hour stirring period, additional deionized water was added as required such that the total volume of deionized water and acetic acid added was equal to 2.0 liters. An aliquot for analysis of purgeable organic compounds was collected and refrigerated prior to analysis. The remaining sample was centrifuged and an aliquot was taken for semi-volatile organic analysis from the centrifugate and refrigerated until extraction with methylene chloride. Samples for metals analysis were taken after pressure filtration through a 0.45 micron Millipore membrane filter. Nitric acid (Ultrex^R grade) was added to the samples for metals analysis to yield a pH less than 2. If the dilution was greater than one percent, the dilution was recorded and the data were adjusted accordingly. No refrigeration was required.

Sample generation using the NBS tumblers was essentially similar to that used with the stirrer assembly. One exception was the substitution of a glass bottle with a Teflon^R-lined screw cap (1.8 or 2.3-liter capacity) for the stainless steel beaker. Samples were tumbled for 20 ± 2 hours. If the standard EP was being followed, the pH was adjusted periodically throughout the extraction to pH 5 using 0.5 N acetic acid except that in no case was more than 4 ml of acid per gram of sample added. However, for all other extractions, the leaching medium was added directly to the waste in a 1:20 ratio of mass of waste to leachate volume and no additional leaching medium was added during the extraction.

This latter leaching procedure, the product of the research effort, is presented in numbered format in Appendix A.

Procedures for Inorganic Analyses

Analysis for inorganic constituents was performed by two techniques; atomic absorption spectroscopy (AAS) and inductively coupled argon plasma spectroscopy (ICAP). Because of the relatively high detection limits required for the leachate analyses, all AAS work was performed using flame atomization. In the total content analyses conducted in Task 6, however, the method of graphite furnace atomization was used for some metals present at very low levels. All mercury analyses were conducted using the cold vapor flameless atomic absorption method.

Instrumentation

Two atomic absorption spectrometers were used for the AAS analysis, a Perkin-Elmer Model 603 and a Perkin-Elmer Model 5000. Both units are equipped with deuterium arc background correction capability which was used for all analyses. These microprocessor-equipped units permit standardization with direct readout in concentration units. Hollow cathode lamps were used for all elements except arsenic, selenium, antimony, and thallium where electrodeless discharge lamps were used. The mercury analyses were performed on a Perkin-Elmer Model 305-B atomic absorption spectrometer equipped with a cold vapor apparatus.

The ICAP unit used for this study was a Jarrell-Ash Model 965 equipped with 30 channels and the spectrum-shifter background correction attachment. Background correction was employed along with interelement interference corrections for known spectral overlaps. These corrections were automatically performed by the PDP-8A computer interfaced to the spectrometer. Results for 30 elements are printed in concentration units based on the standards run with each set. Background and interelement corrections used are specific for each ICAP unit since the configuration of each instrument (element, wavelength) is unique.

Sample Preparation

Sample preparation for elemental analysis of leachates was based on standard EPA procedures in "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020(42), or on the methods given for the proposed ICAP analysis in the Federal Register (December 3, 1979).

Samples for the analysis of 22 elements (Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Na, Sb, Sn, Ti, V, Y, Zn) by either AAS or ICAP were prepared using Method 4.1.3 from "Methods for Chemical Analysis of Water and Wastes"(42). This procedure involves the vigorous digestion of a sample aliquot with nitric acid and incorporates a repeated refluxing of the sample until digestion is deemed complete. This procedure is essentially identical to the ICAP digestion procedure (8.3) given for total metals in the cited Federal Register.

For analysis of four other elements (Se, Tl, Ag, As,) a second digestion procedure was used, involving the use of nitric acid and hydrogen peroxide in a less vigorous procedure(44). This sample preparation was used for the analysis of the listed metals by ICAP or AAS, as required.

Studies conducted for this program indicated no loss of added spike of the above elements using Method 4.1.3, as long as care was taken not to take the sample to complete dryness on heating. However, better spike recoveries were obtained for antimony using the nitric-hydrogen peroxide acid digestion than for the HNO_3 procedure. In the latter stages of the project, only Method 4.1.3 was used for the preparation of samples.

The digestion procedure used for mercury analysis is given in "Methods for Chemical Analysis of Water and Wastes"(42). The organomercury compounds are first subjected to a H_2SO_4-HNO_3 digestion. The mercury is oxidized by the addition of permanganate and persulfate, with the excess reduced with hydroxylamine. Finally, stannous sulfate is used to reduce mercury to the elemental state and the mercury is aerated from solution in a closed system into a cell positioned in the light path of an atomic absorption spectrophotometer. The elemental mercury vapor absorbs the radiation of the mercury hollow cathode lamp that is passed through the cell.

PROCEDURES FOR ORGANIC ANALYSES

Volatile Organic Analysis

Analyses of the organic compounds in the solid waste leachates were conducted for volatile organic and semivolatile organic constituents. The volatile components were analyzed by EPA Method 624(43). A 5-ml aliquot of the leachate sample for purgeable organic analysis was spiked with a three-component internal standard and transferred to the analytical system consisting of:

- A Tekmar Model LSC-1 Liquid Sample Concentrator fitted with a 5-ml sample container and a 12-inch adsorbent trap containing 15.2 cm of Tenax and 8.2 cm of silica gel
- A GC equipped with a 2 meter x 2 mm I.D. glass column packed with 1 percent SP-1000 on 60/80-mesh Carbopak B, and
- A quadrupole mass spectrometer (Finnigan Model 3200). The mass spectrometer was controlled by an INCOS data system. The mass range of 40 to 280 a.m.u. was scanned during the data acquisition.

Only selected leachates were screened for volatile organic components since the semivolatile constituents were more important for assessing potential mobility.

The volatile organic analysis of solid waste leachates for the interlaboratory comparison study (Task 6) was performed using a carbon disulfide extraction procedure. A 40-ml aliquot of leachate was placed in a separatory funnel and extracted with 2 ml of carbon disulfide (CS_2) and 20 ul of methanol containing 200 µg of 1,2-dichloropropane which served as the internal standard. The mixture was shaken for one minute and allowed to stand for 15 minutes before an aliquot of the CS_2 extract was withdrawn for analysis by gas chromatography. A Hewlett-Packard Model 5700 GC with an FID detector was used for analysis of the CS_2 extract using a 30-m SP-2100 glass capillary column. The column temperature was programmed from -10°C to 200°C at

8 degrees per minute. The linear velocity through the column was 50 cm/sec using hydrogen as the carrier gas.

The volatile organic content of solid wastes was determined by extracting a 2-gram sample (wet weight) with 2 ml of CS$_2$, 20 ml of water, and 20 1 of methanol containing the internal standard (1,2-dichloropropane). Sample agitation and elapsed time during the sample transfer step were minimized to avoid loss of volatile compounds. A 50-ml centrifuge tube was used for the extraction and capped immediately following addition of the waste and extraction media. The tube was shaken vigorously for 1 minute, centrifuged for 15 minutes, and an aliquot withdrawn by syringe for GC analysis. The GC conditions were identical to those described for leachate analysis except that the column temperature was raised to a higher temperature (250°C) to elute high-boiling components.

Semivolatile Organic Analysis

The method used to analyze the leachates for semivolatile organic compounds is a modified version of EPA Method 625(43). A 300-ml aliquot of leachate was placed in a 500-ml bottle having a Teflon^{R}-lined screw cap and shaken with 30 g of NaCl until the NaCl was dissolved. The pH was adjusted with 6N HCl to less than 2 and the sample was cooled to less than 28°C prior to completely transferring the solution to a 500-ml separatory funnel. The sample bottle was rinsed with 150 ml of methylene chloride which was added to the separatory funnel. The separatory funnel was shaken vigorously for 2 minutes. A 100-ml aliquot of the methylene chloride extract representing 200 ml of leachate was dried and concentrated to 2 ml using the procedures described in EPA Method 625. The concentrate was transferred to a 2-ml septum-capped vial and mixed with 50 1 of methanol containing 100 µg of D$_{10}$-anthracene as an internal standard for the GC-MS analysis.

Due to the large number of extracts requiring GC-MS analysis for semivolatile organic compounds, an automatic sample injection system was used. A Finnigan 4000 GC-MS with INCOS Data System was equipped with a Hewlett Packard Model 7672A autosampler. The computer compound search and quantification procedure utilized both the Finnigan INCOS computer programs, computer programs for the OWA Finnigan GC-MS System, and programs developed at Battelle. The GC-MS analyses were performed using a 30-meter SE-52 Methyl silicone capillary column programmed from 50°C (2 minutes hold) to 300°C (5.5 minutes hold) at the rate of 4°C/min. The injector temperature was 270°C while both the separator oven and transfer line were maintained at 280°C. The mass range from 70 to 450 a.m.u. was scanned at a rate of 2 seconds per scan.

The mass spectra for compounds identified and quantified using the automated search routine were also examined for accuracy by experienced mass spectrometrists.

STATISTICAL CONSIDERATIONS

During the preliminary planning stages of this method development program, the use of formally designed experiments required for rigorous statistical comparisions between the methods was ruled out because it was not considered possible to identify and control all of the significant variables that might be involved. Also due to the complexity and size of this project, time and cost considerations precluded the use of such designs. In addition, it was believed that secondary characteristics of the methods, such as the biological effect of the leaching medium, were important properties which had to be considered in any comparison among methods. Only more extensive experiments could provide rigorous information on these secondary characteristics. Therefore, the comparisons made between various methods and the choice made for candidate methods were based to a significant degree on sound scientific judgment.

However, the primary characteristics of concern were the reproducibility of the individual method, i.e., the reproducibility of the amount of material leached from a waste, and the analytical precision of the associated measurement process. Qualitative comparisons of measures of reproducibility and analytical precision obtained from the experimental data rather than strict quantitative comparisons were made. Therefore, it was decided to collect the precision data for the various leaching methods using individual experiments based on the sound analytical principles of analyzing blanks, real samples and spiked samples using replications. During the initial planning, it was decided that five replications should be used in each of the experiments. The choice of five was not based on any objective statistical criteria, but rather on the basis that five replications should provide sufficient information on the sources of variability to qualitatively compare the methods. During the course of the program, it became evident that the difference in potential mobility observed for the media examined were sufficiently great that means rather than coefficients of variation could be used for comparison. It was therefore decided to reduce the number of replications to three. In view of the fact that comparisons among methods in terms of precision were made in a qualitative way, and that the analytical method repeatabilities were grossly smaller than the repeatability of mobility of different leachate media, the use of three replications was judged to be adequate.

The decisions about the relative behavior of the various leaching methods applied to the various sample wastes were based on several basis summary statistics and sound scientific judgment. The basis summary statistics included average background, average observed spike value, percent spike recovery, standard deviations and relative standard deviations. The scientific judgment required to assess the important qualitative characteristics of the leaching methods was provided by Battelle scientists.

QUALITY ASSURANCE

The quality assurance activities of this program were those associated with experimental design, sample tracking, documentation, and analytical quality control.

Experimental Design

The considerations for experimental design were based on the program objective of developing a technically sound, practical waste leaching procedure that will simulate natural leachability and will be within the capabilities of a production-type laboratory. In addition, the experimental design was controlled by the significant number of experiments to be accomplished in a short time (6 months).

The leaching procedures were compared in various ways, as described in other sections of this report, and much of the comparison was in terms of amount leached and repeatability of the amount leached. Thus, in effect, the comparisons made were results of analytical determinations of selected metals and organic compounds in leachates.

In order to assess the variability contributed by the leaching process including any effect contributed by sample inhomogeneity, it was necessary to determine the variability contributed by the analysis process. This task was accomplished by conducting replicate analyses of spiked distilled water standards. Statistical analysis of these data included relative standard deviation and percent recovery for inorganic and organic compounds of interest added at three concentration levels.

Documentation

Documentation included sample identification and tracking, sample labeling, and experimental records. Because of the large number of leachates to be generated, a carefully designed sample logging and tracking system was implemented in order to ensure an efficient and accurate flow of samples through the many steps of the procedure. Upon receipt, each waste sample was assigned a unique laboratory identification number which was recorded in a master laboratory record book (LRB). Laboratory record cards were prepared and are permanently filed by project number with cross references to all laboratory notebooks used.

Since the project involved repeated use of the same waste with as many as seventeen different leaching media, further identification had to be provided to eliminate any ambiguity. Thus, each individual leachate was assigned a unique identifier code. This code was based on the laboratory record book number and page number on which that experiment was permanently recorded. All replicates were recorded on the same page and were assigned sequential numbers. For example, 35704-16-3 refers to a particular leachate with all conditions recorded in laboratory record book 35704 on page 16. The -3 indicates this leachate is the third replicate. On that page are recorded all pertinent information including what waste sample was leached, the leaching solution used, the extractor used, the initial and final pH of the leachate, and any other observations for that sample.

Three separate samples were obtained from each leachate generated and analyzed for metals, volatile organic compounds, and semivolatile organic compounds, respectively. For metals and volatiles analyses, the leachate number was adequate identification. For semivolatile organic analysis each sample required a solvent extraction prior to analysis. Each extract was assigned an additional number according to the lab book in which the extraction was recorded. The leachate numbers were cross-referenced in this book.

As implied above, documentation included a record of all experimental work done and all resulting data. Data that resulted from a print-out from an instrument are filed and identified to refer to a laboratory record book where the experiment is described. The filed print-out can also be traced from information in LRBs. The LRBs used in this program are numbered 35692, 35704, 35785, 35900 and 36125. These books are part of the permanent program file.

Data report forms were designed clearly and completely to identify the data in terms of sample, sample type, sample number, leaching media, leaching method, spike level, replication number and analysis method. The data on these forms were entered into the computer where means, precisions and recoveries were calculated. Before doing any calculations, a computer print-out was compared to data on the data sheets to ascertain completeness and accuracy. The results of computer calculations were verified to be true and accurate by comparison to results of manual calculations on a set of data.

Analytical Quality Control

Analytical quality control (QC) included use of approved methods previously published by the EPA(42-45). The quality control recommendations found in the referenced documents were followed in addition to general Battelle QC procedures.

Specifically QC activities consisted of daily calibration of equipment, daily analysis of blanks, periodic use of QC standards (one standard for every four samples for organic determinations and one standard for every seven samples for metals determinations) and daily use of decafluorotriphenyl phosphine (DFTPP) to check the tuning of the quadrupole mass spectrometer.

At the beginning of the method development program, precision was determined for each analysis method utilized. These precision data were useful in setting criteria for performance of QC standards and as a basis of comparison for results of leaching experiments. In the case of metals analyses, the result was expected to agree within 5 percent relative to the expected value--otherwise the system was recalibrated. For organic analyses the calculated reponse factor of a check standard was expected to agree within three standard deviations of the expected reponse factor. If not within that range the system was recalibrated. The results of these controls and checks are part of the documented experimental effort.

Reagent chemicals used in this program were analytical grade or distilled in glass and while purity was not checked on individual chemicals, the purity was verified to be appropriate through results of method blank determinations.

Standards used for the inorganic analyses were obtained from two different sources--Fisher Scientific and Spex Industries, Inc. Each standard solution used in this program was prepared individually by dilution of a Fisher stock solution (not serially diluted to obtain various concentrations) and compared periodically to standards prepared from Spex high purity solids (> 99.99 percent pure).

Calibration standards were prepared biweekly from stock solutions which were checked for contamination from other elements by ICAP. A solution containing the same element prepared using Spex solid standards was also analyzed by ICAP. Contamination was verified if only one of the standards produced a signal for some other element. However, an interelement interference was identified if both standards produced a signal for some element of the same apparent concentration. Interelement interference corrections were based on three determinations at a single concentration level shown to be within the linear range for that element.

Standards for organic analyses were obtained from many sources. These compounds were kept in a locked repository and the purity was monitored by various techniques depending on the use. A record was kept for each reference compound that includes source, date of purchase, and purity information. The purity information included when purity was monitored, the method of monitoring and the results. Primary stock standard solutions were made from these pure compounds by dissolving a known mass of the compound in a known volume of solvent. These stock standards were diluted to achieve appropriate concentrations.

Inorganic Analysis Routine

To verify that an instrument was operating correctly and within the expected performance limits, an appropriate standard was included within every seven samples. For ICAP analysis of standard solutions, the determined values agreed with the known concentration of the standard within ± 5 percent. If the value obtained was outside these limits, the instrument was restandardized prior to continuing the analyses. Any samples analyzed after an acceptable standard check and before the unacceptable check were repeated. An identical protocol was used for flame atomic absorption using single element standards rather than the multi-element standards used for ICAP. For flameless atomic absorption, the acceptable limits for standard checks were ± 10 percent, due to the less precise nature of these analyses.

Spiked samples, with the spike added prior to sample preparation, were prepared and analyzed with each set of replicates for a given waste and leachate combination. The samples to be spiked were selected randomly. For all ICAP and atomic absorption analyses, the spike recoveries were expected to be within 100 ± 10 percent of the amount added, where spike recovery was calculated by

$$\frac{\text{(sample + spike added) - (sample)}}{\text{spike added}} \times 100\%$$

However, for flameless AA analyses used in the total content determinations, the method of standard additions was used in all cases as required in the method. Each leachate was prepared in quintuplicate or triplicate thus, no further replication was required.

Standard solutions prepared from dilutions of commercially available stock solutions were used for calibration of all instruments. As an additional check on standard purity, stock solutions were compared periodically from two different sources (Fisher Scientific or Spex Industries, Inc.). All required standards from both sources were available in the laboratory since all of these analyses are routinely performed at Battelle.

To properly exercise the power of simultaneous, multi-element analysis by ICAP, special precautions were required. These included the recognition and correction of interelement interferences and the use of background correction. Both procedures are routinely employed in the laboratory.

Similarly, fundamental knowledge of atomic absorption principles and techniques were required to produce valid results, especially when graphite furnace work was required. The experience in this laboratory is extensive with both ICAP and AAS, and enabled the strict adherence to the Quality Assurance plan.

The studies for precision and accuracy of metals analyses were done using one operator for each step. That is, a different person was responsible for each of the following steps: preparation of calibration standards, preparation of spiking solutions, generation of leachates, sample digestion, ICAP analysis, and AAS analysis. An exception to this scheme was for the analysis of mercury in which case one operator carried out all steps except the leachate generation. Observation and supervision of the whole process, from formulation of standards to data review and management, was the responsibility of one professional chemist.

Standards, leachates and spikes were prepared and analyzed over a period of several days. The order of analyses was randomized so each days run included all concentration levels. The results of all QC determinations were reported along with the associated data set.

Organic Analysis Routine

High concentrations of some purgeable compounds may cause carryover from one sample to the next sample, invalidating the data for the next analysis. This situation occurred for the organic still bottom leachate sample. To analyze a method blank following each sample would be costly and impractical for such a heavy sample load.

For determination of purgeable compounds the routine procedure adopted was to alternate the Tekmar glass fit after each run. After running a sample and emptying the sampler, the sampler was rinsed with methanol and distilled water, and dried in a glassware oven at 100°C. Another sampler which had been drying in the oven was used for the next run. The sampler was cooled before attaching it to the Tekmar Liquid Sample Concentrator and adding the next sample.

In order to insure quality control, the following procedures were used on a daily basis:

(1) Instrument checked (Finnigan 3200), tune with FC-43 calibration compound.

(2) Instrument calibrated (m/e 20-510; 2.95 sec up, 0.05 sec down, scan parameters).

(3) Method blank analyzed (5.0 ml freshly purged water plus 5.0 µl spike of the 50 ng/ µl three-component internal standard solution (50 ppb; m/e 46-260 scan range for the sample runs).

(4) A spiked 100 ppb standard solution was analyzed.

(5) The next four samples, spiked at the 50-ppb level with the three-component internal standard solution were analyzed.

(6) Another spiked standard containing 20 ppb of the 27 compounds of interest was analyzed.

(7) The next four samples were analyzed followed by another standard at the 100-ppb level.

For the GC-MS analysis of samples for semivolatiles samples were run in the following sequence (1.0 µl injected):

80 ng/µl standard
4 samples
20 ng/µl standard
4 samples
80 ng/µl standard
4 samples
200 ng/µl standard
4 samples
REPEAT SEQUENCE

This sequence allowed for analysis of an 80 ng/µl standard every eight runs and permitted 16 samples to be analyzed for every 20 runs. Response factors (RFs) were recalculated for each standard run and the data were tabulated. The RF from the 80-ng standards was used to quantify the sample components. The analysis methods precision studies were conducted over a period of two days while the precisions calculated during sample analyses encompass a period of four weeks. The operation of the instruments was done by a single analyst while standards were made and samples prepared by several other operators.

Precision and accuracy were assessed first of all for the analytical method through replicate analyses of standards carried through the analysis procedure. Precision was calculated as relative standard deviation as follows:

$$S = \text{Standard Deviation} = \left[\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}\right]^{1/2}$$

$$x = \text{Mean} = \frac{\sum_{i=1}^{n} x_i}{n}$$

$$\text{RSD} = \text{Relative Std Dev} = \frac{S}{\bar{x}} \times 100.$$

Accuracy was calculated in terms of percent recovery of a compound added (spiked) to water and leachates as follows:

$$\text{Percent Recovery} = \frac{(\text{sample + spike}) - (\text{sample})}{\text{spike}} \times 100 \quad .$$

Secondly, the protocol of leaching included replicate leachings of the same waste with the same leaching medium. The results of analyses of these replicated leaching solutions were used to estimate the repeatability of leaching by calculation of relative standard deviation as above. In addition, one of the replicated leaching solutions was spiked with compounds and metals of interest in order to calculate a percent recovery also as above. The replicated leachings thus provided information on the effect of the leached materials on analytical performance.

SECTION VI

RESULTS

SAMPLE CHARACTERIZATION

The pH and percent solids content of each waste were determined upon receipt as part of Task 1. These results and the classification codes assigned to each waste have already been given in Table 3. The physical compatibility assessments of each waste for the leaching processes (centrifugation, filtration, stirring, tumbling) are reported in Table 4. Also included is a description of each waste according to appearance (color, solid content).

SAMPLE SELECTION

From a total of 23 waste samples collected, eight samples were initially selected for further study:

- Latex paint
- Still bottoms
- Baghouse dust
- Coal gasification tar
- Ink pigment
- POTW dewatered sludge
- Herbicide acetone and water
- Herbicide acid

The criteria for selection of the wastes included:

(1) Estimation of organic content and variety of organic compounds expected
(2) Range of pH
(3) Range of solid content
(4) Complexity of matrix from both physical and chemical considerations
(5) Category of waste

When the herbicide acetone and the herbicide acid were mixed with water for the initial leaching experiments, it was found that both were completely soluble. Thus, these two wastes were eliminated from consideration and the pharmaceutical waste was substituted for study. It was anticipated that the latex paint sample would be high in organic content. Since this sample proved to be low in organic content, no further analyses were performed.

TABLE 4. PHYSICAL CHARACTERISTICS OF WASTE SAMPLES

Sample	Category (a)	Amenability to Given Processing Technique[b] Centri-fugation	Filtra-tion	Stirring	Tumbling	Physical Description of Sample
Raw POTW	AS	✓	No	✓	✓	Thin dark green aqueous suspension
Dewatered POTW	IS	✓	✓	✓	✓	Dark wet cake
Electroplating	IS	✓	✓	✓	✓	Dark wet cake
Latex Paint	AS	✓	No	✓	✓	Thick milky aqueous suspension
Lime Slurry	AS	✓	✓	✓	✓	Thin tan aqueous suspension
Food Processing	AS	✓	✓	✓	✓	Thin tan aqueous suspension
Coke Plant	AS	✓	✓	✓	✓	Thin dark aqueous suspension
Still Bottoms	OS	✓	✓	No	✓	Thick black chunky aqueous slurry
Fly Ash	IS	✓	✓	✓	✓	Fine tan powder
Baghouse	IS	✓	✓	✓	✓	Fine dark brown powder
Pulp/Paper	OS	✓	✓	✓	✓	Brown wet fibrous lumpy cake
Coal Tar	OS	No	No	No	✓	Black viscous tar with water layer
Oil Refining	OW	✓	No	✓	✓	Medium viscosity dark oil with sediment
Machine Op.	OW	✓	No	✓	✓	Brown oil-water mixture ∿25% oil
Ink Pigment	AS	No	No	✓	✓	Pourable black jelly
Pickle Acid	AS	✓	✓	✓	✓	Thin brown aqueous suspension
Alkaline	AS	✓	✓	✓	✓	Thin tan aqueous suspension
Engine Mfg	AS	✓	No	✓	✓	Thin gray aqueous suspension with oil
Water Treatment	AS	✓	No	✓	✓	Thick brown aqueous suspension with granules
Herbicide-Acetone	AS	✓	✓	✓	✓	Dark red-brown aqueous solution
Herbicide-Acid	AS	✓	✓	✓	✓	Thin gray aqueous suspension
Paint Mfg	AS	✓	No	✓	✓	Thin milky gray-green aqueous suspension
Pharmaceutical	AS	✓	No	✓	✓	Gelatinous red-brown stinky, aqueous suspension

(a) AS = aqueous sludge (>80% H_2O); OW = oily waste (>20% oil); IS = inorganic solid (>20% inorganic); OS = organic solid (>20% organic).

(b) Check mark indicates "yes".

EXTRACTOR EVALUATION (TASK 3)

The two extractors, ADMCo stirrer and NBS tumbler, were used in a parallel leaching experiment to determine if any differences in the analytical results would be obtained. The dewatered POTW sludge was leached using the EP medium and the leaching methods described previously. Five replicate extractions and a blank were processed using both techniques. The leachates were analyzed for both organic and inorganic constituents. The average and standard deviation for each analyte found in significant quantities are presented in Table 5. The metal analysis data for the NBS tumber are generally more precise than for the ADMCo extractor. For the analysis of 22 elements leached using the ADMCo unit, the average relative standard deviation was 37 percent, while for the NBS tumbler the average RSD for the same 22 elements was 28 percent. Significant losses of volatile organic compounds, such as toluene, chlorobenzene, and ethylbenzene, occurred when the ADMCo extractor was used. Comparable results were obtained for less volatile compounds such as phenanthrene.

Based on the analytical results obtained for Task 3 and the simpler operation of the NBS tumbler, only the NBS tumbler was used for leaching method development in Tasks 4 and 5.

EFFECT OF MEDIA (TASK 4)

The objective of this task was to compare the effectiveness of various aqueous media for leaching organic components as well as inorganic components from a solid waste sample. The solid waste sample chosen for this task was a chemically dewatered municipal sludge sample (POTW sludge) having a solids content of 25 percent. This sample was chosen since it was known to contain significant levels of a wide range of organic compounds as well as metals. Several aqueous media (listed in Table 6) having widely varying chemical characteristics (pH, ionic strength, surfactant levels, and oxidation potential) were evaluated. Since the focus of this study was on codisposal of wastes, rather than monodisposal, slightly acidic (pH 4-6) media were selected. Distilled water was also evaluated as a reference point for comparison of data.

The data obtained are given in Table 7 and the precision of the replicate leachings is given in Table 8. Organic components present in the leachate from POTW sludge included toluene, chlorobenzene, ethylbenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, acenaphthene, fluorene, phenanthrene, and various phthalates. No phenols were found in the leachates above the detection limit (~50 µg/liter).

Examination of the data in Table 7 reveals that the only significant effect of leaching medium on mobility of organic compounds is the somewhat greater leaching ability of citrate relative to both distilled water and acetate buffer. The POTW sludge used contained very high levels of iron resulting from chemical dewatering with ferric chloride and lime. The citrate-containing leaching media gave leachates containing extremely high levels of iron, nearly 0.1 percent. The high levels of the ferric citrate

TABLE 5. DATA FOR EXTRACTOR EVALUATION -- TASK 3

Analyte	Amount of Analyte Found, μg/l, Using Given Extractor	
	ADMCO	NBS
Al	440 ± 190	860 ± 540
B	210 ± 54	390 ± 100
Ba	930 ± 450	1200 ± 170
Cd	42 ± 18	63 ± 15
Co	57 ± 24	71 ± 11
Cr	94 ± 26	120 ± 54
Cu	37 ± 11	66 ± 24
Fe	3700 ± 2000	6700 ± 7400
Pb	110 ± 62	170 ± 71
Mn	3200 ± 1700	4100 ± 580
Mo	47 ± 26	36 ± 4
Ni	580 ± 300	670 ± 130
Na	15500 ± 1200	16000 ± 1700
Sn	120 ± 22	130 ± 16
V	44 ± 10	47 ± 6
Y	18 ± 10	43 ± 16
Zn	2300 ± 1200	3300 ± 910
Se	90 ± 53	120 ± 23
Tl	670 ± 100	830 ± 91
Ag	9 ± 2	12 ± 4
As	210 ± 51	250 ± 43
Sb	98 ± 22	110 ± 16
Toluene	1.5 ± 0.3	61 ± 7
Chlorobenzene	0.4 ± 0.1	29 ± 4
Ethylbenzene	1.5 ± 0.4	34 ± 7
1,4-Dichlorobenzene	4 ± 1	34 ± 24
1,2,4-Trichlorobenzene	100 ± 33	180 ± 18
Naphthalene	10 ± 3	25 ± 3
Acenaphthene	3 ± 1	2 ± 1
Fluorene	2 ± 1	1 ± 1
2,4-Dinitrotoluene	7 ± 4	10 ± 6
Phenanthrene	13 ± 4	16 ± 2
Dibutyl Phthalate	230 ± 40	250 ± 63
Bis(2-ethylhexyl) Phthalate	12 ± 7	20 ± 6

TABLE 6. DESCRIPTION OF LEACHING MEDIA

Medium	Contents per Liter of Medium[a]
EP Acetic Acid Titration	0 to 400 ml acetic acid
0.1M Sodium Acetate, pH 4	5.7 ml acetic acid and 8.2 g sodium acetate
0.1M Sodium Citrate, pH 4	21 g citric acid monohydrate and 4.8 g sodium hydroxide
0.1M Sodium Citrate, pH 5	21 g citric acid monohydrate and 8 g sodium hydroxide
0.05M Sodium Hydrosulfite	8.7 g sodium hydrosulfite
0.05M Sodium Citrate, pH 4	10.5 g citric acid monohydrate and 2.4 g sodium hydroxide
0.1M Ammonium Citrate, pH 4	8.6 g citric acid monohydrate and 13.3 g ammonium dibasic citrate
0.1M Sodium Butyrate, pH 4	8.8 g butyric acid and 0.7 g sodium hydroxide
0.02M Ferrous sulfate and 0.1M Sodium Citrate, pH 5	21 g citric acid monohydrate, 5.6 g ferrous sulfate heptahydrate, and 9.4 g sodium hydroxide
U Wisc Synthetic Leachate	1.05 g pyrogallol, 6.9 g ferrous sulfate heptahydrate, 20.4 g sodium acetate trihydrate, 8.6 ml acetic acid, and 3.8 g glycine
0.05M Sodium Hydrosulfite, and 0.1M Sodium Citrate, pH 5	8.7 g sodium hydrosulfite, 21 g citric acid monohydrate, and 16.7 sodium hydroxide
0.01% Igepal	0.1 g Igepal CO-630[b]
0.01% Igepal CO-630, and 0.1M Sodium Citrate, pH 5	0.1 g Igepal CO-630, 21 g citric acid monohydrate, and 8 g sodium hydroxide
0.05M Sodium Citrate, pH 5	10.5 g citric acid monohydrate and 4 g sodium hydroxide
0.02M Sodium Citrate, pH 5	4.2 g sodium citrate monohydrate and 1.6 g sodium hydroxide
0.01% Igepal, and 0.05M Sodium Citrate, pH 5	0.1 g Igepal CO-630, 10.5 g citric acid monohydrate, and 4.0 g sodium hydroxide
0.05M Sodium Hydrosulfite and 0.05M Sodium Citrate, pH 5	8.7 g sodium hydrosulfite, 10.5 g citric acid monohydrate, and 4.0 g sodium hydroxide

(a) Distilled, deionized water used to prepare all media.
(b) Igepal CO-630 is a registered trademark of GAF Corporation.

TABLE 7. COMPARISON OF LEACHATES FROM DEWATERED POTW SLUDGE

Analyte	Analysis Method	Amount Found[(b)] Using Distilled Water, µg/ℓ	Relative Amount[(a,b)] Found Using Given Leaching Medium[(c)]															
			EP	0.1M NaOAc pH 4	0.1M NaCit pH 4	0.1M NaCit pH 5	0.05M $Na_2S_2O_4$	0.05M NaCit pH 4	0.1M NH_4Cit pH 4	0.1M NaOBu pH 4	$FeSO_4$ 0.1M NaCit pH 5	U Wis SL pH 4.5	$Na_2S_2O_4$ 0.1M NaCit pH 5	0.01% Igepal CO-630	Igepal 0.1M NaCit pH 5	0.05M NaCit pH 5	0.02M NaCit pH 5	$Na_2S_2O_4$ 0.05M NaCit pH 5
Al	ICAP	480	1.6	0.5	106	89	0.2	89	108	0.7	93	27	100	0.5	100	71	0.4	91
B	ICAP	46	8.5	4.1	15	13	3	12	13	4.6	22	6.5	24	1.2	22	18	6.8	28
Ba	ICAP	70	17	17	40	60	0.3	23	49	16	21	2.6	21	8.1	55	23	8.9	27
Co	ICAP	7	10	9.2	24	23	2.8	20	23	8.9	13	2.8	23	ND	21	16	2.0	37
Fe	ICAP	2000	3.3	2.3	265	252	1.1	235	240	1.4	(d)	(d)	220	0.3	220	175	13	250
Mn	ICAP	35	117	109	146	143	29	131	140	114	150	128	143	0.6	143	117	26	157
Mo	ICAP	57	0.6	0.7	5.6	5.3	2.3	4.6	5.3	1.0	4.2	2.5	6.1	1.1	5.6	5.1	1.7	6.3
Sn	ICAP	21	6.2	5.7	56	41	4.3	34	54	7.1	40	20	48	0.9	52	37	4.1	74
Cd	ICAP	<5(e)	13	7	20	17	3	11	20	5	ND	22	32	ND	18	ND	3	33
Cd	FAAS	<20(e)	3	2	5	3	ND	2	6	1	ND	3	6	ND	3	ND	NA	NA
Cr	ICAP	29	2.9	3.1	131	124	2.5	106	124	3.8	131	31	134	0.7	131	37	4.3	143
Cr	FAAS	<100(e)	ND	ND	45	58	ND	35	40	ND	53	13	39	ND	37	27	NA	NA
Cu	ICAP	53	0.9	0.5	6.0	13	0.3	5.0	10	0.5	ND	ND	42	0.2	8.9	6.8	0.1	25
Cu	FAAS	<50(e)	2	ND	6	14	ND	5	10	9	2	ND	44	ND	11	8	NA	NA
Pb	ICAP	88	1.9	0.9	86	78	0.7	53	91	1.6	5.3	16	91	ND	91	24	0.9	80
Pb	FAAS	<200(e)	ND	ND	49	44	ND	29	38	ND	ND	6	39	ND	39	8	NA	NA
Ni	ICAP	<50(e)	13	12	24	22	2	20	26	12	17	26	30	ND	26	16	0.8	2.8
Ni	FAAS	<100(e)	8	7	14	13	ND	11	13	6	8	10	14	ND	12	7	NA	NA
Zn	ICAP	63	51	37	95	85	ND	69	92	25	14	73	122	3.8	82	17	7.4	182
Zn	FAAS	73	45	36	90	79	0.3	63	85	22	36	70	103	2.9	75	15	NA	NA
Tolu[(f)]	GC-MS	65	0.9	0.8	0.6	NA	NA	0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ClBz	GC-MS	33	0.9	0.8	0.6	NA	NA	0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
EtBz	GC-MS	33	1.0	0.8	0.8	NA	NA	0.6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
pDCBz	GC-MS	20	1.7	1.0	1.5	1.6	0.9	1.4	1.3	NA	1.3	1.1	0.7	1.2	2.9	2.2	NA	NA
TCBz	GC-MS	180	1.0	1.0	2.4	2.8	0.8	2.8	2.2	NA	1.9	1.2	1.2	1.0	5.6	2.8	NA	NA
Naph	GC-MS	27	0.9	0.9	1.2	1.2	0.9	1.1	1.0	NA	0.9	0.7	0.4	1.0	2.4	1.4	NA	NA
Acne	GC-MS	3	0.7	0.7	3.0	3.3	3.0	2.7	2.0	NA	2.0	0.7	2.0	ND	8.3	2.0	NA	NA
Fluo	GC-MS	3	0.3	1.0	1.3	1.7	1.0	2.3	1.3	NA	1.0	0.7	0.7	1.0	4.3	4.0	NA	NA
Phen	GC-MS	15	1.1	1.0	3.5	4.0	0.7	4.4	3.3	NA	2.4	0.9	2.1	0.9	10	3.7	NA	NA
BEHP	GC-MS	16	1.3	1.0	7.5	1.6	0.5	12	8.1	NA	7.5	1.1	6.3	1.1	31	33	NA	NA

(a) Relative to the amount found using distilled water.
(b) Average of five runs.
(c) More complete descriptions of leaching media are given in Table 6.
(d) High blank value interfered with the determination.
(e) Relative amounts based on detection limit for these elements.
NA = Not analyzed. ND = Not detected.

(f) Tolu - toluene
ClBz - chlorobenzene
EtBz - ethylbenzene
pDCBz- 1,4-dichlorobenzene
TCBz - 1,2,4-trichlorobenzene
Naph - naphthalene
Acne - acenaphthene
Fluo - fluorene
Phen - phenanthrene
BEHP - bis(2-ethylhexyl) phthalate.

TABLE 8. PRECISION OF ANALYSIS OF LEACHATES FROM DEWATERED POTW SLUDGE

Analyte	Analysis Method	Percent Relative Standard Deviation[a] of Amount Found Using Given Leaching Medium[b]															
		H_2O	EP	0.1M NaOAc pH 4	0.1M NaCit pH 4	0.1M NaCit pH 5	0.05M $Na_2S_2O_4$	0.05M NaCit pH 4	0.1M NH_4Cit pH 4	0.1M NaGBu pH 4	$FeSO_4$ 0.1M NaCit pH 5	U Wis SL pH 4.5	$Na_2S_2O_4$ 0.1M NaCit pH 5	0.01% Igepal CO-630	Igepal 0.1M NaCit pH 5	0.05M NaCit pH 5	0.02M NaCit pH 5	$Na_2S_2O_4$ 0.05M NaCit pH 5
Al	ICAP	54	63	38	5	5	19	4	1	39	4	12	8	96	2	8	10	8
B	ICAP	26	25	10	4	5	5	3	2	7	33	11	13	34	12	10	25	26
Ba	ICAP	34	14	6	4	6	31	9	3	8	3	9	24	49	9	5	8	26
Co	ICAP	14	15	5	5	3	15	0	0	4	7	4	13	ND	6	6	4	17
Fe	ICAP	55	110	77	6	2	60	3	3	83	(c)	(c)	8	128	6	5	20	6
Mn	ICAP	37	14	2	6	4	16	3	3	5	4	3	8	44	5	10	26	6
Mo	ICAP	7	11	10	5	4	5	3	2	14	9	7	10	5	4	12	5	3
Sn	ICAP	29	12	6	3	1	11	5	4	4	14	5	4	14	7	7	7	10
Cd	ICAP	ND	24	16	9	10	21	16	5	18	ND	23	7	6	7	ND	8	25
Cd	FAAS	ND	21	12	13	9	ND	33	9	19	ND	41	11	ND	20	ND	NA	NA
Cr	ICAP	48	45	4	5	4	4	3	2	5	3	6	8	51	5	7	12	6
Cr	FAAS	ND	ND	ND	6	3	ND	4	6	ND	9	7	8	ND	4	7	NA	NA
Cu	ICAP	50	36	12	44	11	58	8	31	56	ND	ND	22	40	32	56	11	7
Cu	FAAS	ND	11	ND	40	8	ND	11	33	36	19	ND	22	ND	32	49	NA	NA
Pb	ICAP	25	42	60	6	5	9	5	4	14	18	7	14	ND	3	15	5	6
Pb	FAAS	ND	ND	ND	5	4	ND	7	6	ND	ND	12	13	ND	3	20	NA	NA
Ni	ICAP	ND	19	4	7	4	19	6	4	6	4	5	7	ND	4	3	4	5
Ni	FAAS	ND	17	5	6	5	ND	3	3	6	7	2	9	ND	4	4	NA	NA
Zn	ICAP	49	28	14	6	4	ND	2	2	27	57	10	6	88	3	13	8	12
Zn	FAAS	30	29	14	5	3	9	2	4	28	42	10	4	81	4	12	NA	NA
Tolu[d]	GC-MS	6	12	9	15	NA	NA	19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ClBz	GC-MS	11	13	4	16	NA	NA	16	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
EtBz	GC-MS	10	19	7	16	NA	NA	9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
pDCBz	GC-MS	13	71	29	10	13	12	10	10	NA	10	12	9	14	25	32	NA	NA
TCBz	GC-MS	8	10	24	7	16	7	15	13	NA	16	21	11	9	30	44	NA	NA
Naph	GC-MS	1	12	25	19	33	4	9	13	NA	7	12	6	5	36	22	NA	NA
Acne	GC-MS	66	50	25	26	30	66	18	42	NA	16	45	33	ND	47	60	NA	NA
Fluo	GC-MS	66	100	33	25	20	33	35	13	NA	23	45	0	20	38	150	NA	NA
Phen	GC-MS	38	16	24	6	20	9	17	14	NA	22	48	10	19	41	64	NA	NA
BEHP	GC-MS	46	32	42	8	30	39	13	12	NA	22	13	11	66	26	120	NA	NA

(a) Average of five runs.
(b) More complete descriptions of the leaching media are given in Table 6.
(c) High blank value interfered with the determination.

NA = Not analyzed   ND = Not detected.

(d) Tolu - toluene
ClBz - chlorobenzene
EtBz - ethylbenzene
pDCBz- 1,4-dichlorobenzene
TCBz - 1,2,4-trichlorobenzene
Naph - naphthalene
Acne - acenaphthene
Fluo - fluorene
Phen - phenanthrene
BEHP - bis(2-ethylhexyl) phthalate

complex may have had more of an effect on the mobility of organic compounds than the citrate itself. The addition of 0.01 percent Igepal (a nonionic surfactant), acetate buffer, or 0.05 M sodium hydrosulfite (a reducing agent) did not alter the mobility of organics relative to that obtained using distilled water. However, the addition of 0.01 percent Igepal in combination with citrate buffer appeared to give a somewhat greater mobility of organics relative to that observed for either Igepal or citrate alone. The effect is best indicated by comparing the results from 0.05 M citrate with those from Igepal plus 0.1 M citrate in Table 7. The extract from the butyrate containing leaching medium could not be concentrated below 10 ml because of the high amount of butyric acid present. GC-MS analysis was not run on the concentrate to avoid contaminating the mass spectrometer. However, GC analysis was conducted and visual examination of the chromatograms revealed that the butyrate gave no significant increase in leachability of organics over the acetate buffer.

The University of Wisconsin "Synthetic Leachate"(17,18) was found to give results for organics similar to both the EP and distilled water, thus indicating that the addition of complexing agents (such as pyrogallol) has little effect on the mobility of organic components.

The mobility of metals from the waste was highly dependent upon the leaching medium composition, as shown in Table 7. Distilled water generally gave the lowest metal levels whereas citrate yielded the highest levels with little effect from the type of cation. The addition of nonionic surfactant (Igepal) predictably had no effect on mobility of metals. The additions of $FeSO_4$ or $Na_2S_2O_4$ (to lower the oxidation potential of the medium) gave no significant increase in metal mobility. Both acetate and butyrate buffer were less effective than citrate in leaching metals. The dewatered POTW sludge formed an alkaline solution when mixed with water, due primarily to the line added in processing. With the EP procedure, the final pH was still 7 after the maximum amount of acetic acid had been added (4 ml of 0.5 N acetic acid/g solid). The distilled water leachate was also alkaline. The final pH of the leachates generated from the buffers of acetate and citrate was generally close to the pH of the buffer. Thus, some of the variation in concentrations observed could be due to a pH effect.

Interference problems were evident for several of the metals (Se, As, Tl, Pb, Ni, and Sb) with samples containing ~500 ppm of Fe or greater, i.e., the citrate leachates. The interference problems arise from the complex emission spectrum from iron, which is difficult to correct when the element is present at high levels. Chemically dewatered sludges generally contain large amounts of iron salts and therefore this problem will be commonly encountered. The use of atomic absorption, rather than ICAP should diminish this problem, although an increase in sample analysis costs will be realized.

Based on the data obtained (Table 7) in this task, seven leaching media were selected for further study (Task 5). These media were:

- Distilled water
- EP acetic acid
- 0.1 M sodium acetate buffer, pH 4

- 0.05 M sodium citrate buffer, pH 5
- 0.02 M Sodium citrate buffer, pH 5
- 0.01 M Igepal + 0.05 M sodium citrate buffer, pH 5
- 0.05 M $Na_2S_2O_4$ + 0.05 M sodium citrate buffer, pH 5

Distilled water and the EP were chosen as reference points, since these media are currently in widespread use in the other laboratories. The 0.1 M acetate buffer (pH4) was chosen because it simulates the EP and gave comparable results to the EP but is much easier to accomplish since titration of the sample to maintain a particular pH level is not necessary. The 0.05 M citrate buffer (pH5) was selected because it was more aggressive than either acetate or distilled water in leaching both organics and metals. It was decided to add 0.02 M citrate buffer to the list (it was not used in Task 4) because it is desirable to reduce the concentration of "additives" to the leaching medium as much as possible. This medium was expected to be more aggressive than acetate but somewhat less aggressive than the higher level citrate buffer and less toxic in bioassay studies.

Although the nonionic surfactant (Igepal) was found to have little effect on mobility of organics from POTW sludge it was selected for further study (organics only) on other wastes since any effect could be highly dependent on the nature of the waste sample (e.g. tars and oils should be more readily extracted into a leaching medium having surfactant present). $Na_2S_2O_4$ was selected for evaluation (in conjunction with citrate buffer) in order to assess the significance of added reducing agent mobility of metals (organics were not determined for this medium) from a variety of waste types.

EFFECT OF WASTE TYPE (TASK 5)

The objective of this task was to evaluate the mobility of organic components and metals from several representative wastes using the leaching media selected on the basis of the data obtained in Task 4. The wastes selected are listed below:

- Baghouse dust
- Still bottoms
- Ink pigment waste
- Pharmaceutical waste
- Coal gasification tar.

The physical nature of these waste samples has been tabulated in this section of the report (Table 5). This group of waste samples was selected for detailed study since these wastes represent a wide variety of waste categories having a range of physical properties.

Baghouse dust was a finely divided solid containing essentially no water and only trace levels of organics. When suspended in water the baghouse dust sample gave a neutral pH. The still bottom sample was a solid residue, high in organic content having approximately 40 percent solids and a pH of 3-4. The ink pigment waste was an alkaline (pH 11) gelatinous material having approximately 15 percent solids and a relatively high level of organics. The pharmaceutical waste was a foul-smelling aqueous sludge having approximately 20 percent solids and a neutral pH. The coal gasification tar was totally organic and approximately 50 percent of the material was volatilized at 100°C overnight (the conditions used to obtain a residue for percent solids determination).

The results obtained for the various leaching media on each waste sample are presented in Tables 9 to 14. The data obtained for each waste are discussed below. The still bottoms leachate contained very large amounts of several chlorinated volatile compounds, as shown in Table 9, and approximately the same levels of these compounds were leached using distilled water and Igepal/citrate buffer. Coal tar leachate contained significant levels of benzene and several alkylated derivatives. Ink pigment leachate contained significant levels of both chlorinated and nonchlorinated volatile organics. Pharmaceutical waste leachate contained only a low level of trichloroethane while latex paint leachate contained low levels of several chlorinated organics.

The leachates from baghouse dust had low levels of four organic priority pollutants (phenanthrene, fluoranthene, pyrene, and phenol) and significant quantities of several metals, especially Al, Ba, Cr, Mn, Mb, Ni, Sn, and Zn. The distilled water leachate gave the highest level of organic compounds except for fluoranthene and pyrene where the Igepal/citrate medium gave larger values. However, the levels of all the organics were quite low and highly variable, making it difficult to assign any significance to the differences observed between leaching media.

In general, the distilled water leachate from baghouse dust contained much lower levels of metals than any of the other leachates (Table 10). The EP gave much higher levels (relative to distilled water) of Mn, Ba, Ni, Sn, and Zn, but actually gave a lower level of Cr. Mb was present at essentially the same level in all leaching media. Acetate buffer (0.1 M, pH 4) gave metal levels comparable to the EP. Both 0.02 M and 0.05 M citrate buffer, pH 5, gave much higher levels of most of the metals, especially Ba, Cd, Cu, Fe, Ni, and Zn, than either the EP or distilled water. The leachate obtained using the higher concentration (0.05 M) citrate contained 2-3 times higher levels of many metals than the leachate obtained using the 0.02 M citrate medium. The addition of hydrosulfite to the 0.05 M citrate medium increased the levels of most metals leached by as much as a factor of two.

The leachates from still bottoms contained significant levels of several organic priority pollutants, as shown in Table 11. In addition, high levels of Al, Ba, Cr, Cu, Fe, Mn, Ni, and Zn were observed. Because the distilled water leachate was acidic (less than pH 5), the EP and distilled water leaching process were identical for this sample. The levels of organics were determined in the EP/distilled water, 0.05 M citrate, and 0.05 M citrate/0.01 percent Igepal. Inspection of the data in Table 11 reveals that citrate, with or without Igepal, gave comparable or lower levels of most organics than distilled water/EP. The only exception was phenol, which was present at a five-fold higher level in the citrate buffer not containing Igepal. However, the high RSD (75 percent) for this value casts considerable doubt on its significance.

TABLE 9. VOLATILE ORGANIC CONTENT OF SELECTED LEACHATES USING EPA METHOD 624

Component	Concentration of Component Found In Leachate From Given Waste Sample, μg/l[c]						
	Latex Paint[a] (H_2O)	Ink Pigment[a] (H_2O)	Pharmaceutical[a] (H_2O)	Still Bottoms[b] (H_2O)	Still Bottoms[b] (Igepal-Cit.)	Coal Tar[b] (H_2O)	Coal Tar[b] (Igepal-Cit.)
Methylene Chloride	14	1,000	ND	100	85	ND	ND
1,1-Dichloroethene	ND	110	ND	11,000	19,000	ND	ND
1,1-Dichloroethane	25	12	ND	130,000	51,000	ND	ND
trans-1,2-Dichloroethene	11	11	ND	78,000	53,000	ND	ND
Chloroform	7	12	ND	17,000	12,000	ND	ND
1,2-Dichloroethane	35	ND	ND	125,000	87,000	ND	ND
1,1,1-Trichloroethane	6	120	12	12,000	19,000	16	15
Carbon tetrachloride	ND	ND	ND	2,300	5,000	ND	ND
Trichloroethene	20	750	ND	80,000	94,000	ND	ND
Benzene	ND	190	ND	17	15	347	375
1,1,2-Trichloroethane	84	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	150	ND	140,000	58,000	ND	ND
Tetrachloroethene	ND	180	ND	22,000	52,000	ND	ND
Toluene	ND	1,850	9	79	86	568	830
Chlorobenzene	ND	15	ND	33	100	ND	ND
Ethylbenzene	ND	1,300	ND	ND	ND	10	14

(a) Single determination.

(b) Average of three determinations.

(c) Leaching medium is given in parentheses.

ND = Not detected.

TABLE 10. COMPOSITION OF LEACHATES FROM BAGHOUSE DUST

Analyte	Amount Found Using Distilled Water		Relative Amount (RA)(a) Found & Percent Relative Std Dev (RSD) Using Given Leaching Medium(b)											
			EP		0.1M NaOAc, pH 4.0		0.05M NaCit, pH 5.0		0.02M NaCit, pH 5.0		0.05M $Na_2S_2O_4$ + 0.05M NaCit, pH 5.0		0.01% Igepal+ 0.05M NaCit, pH 5.0	
	µg/ℓ(c)	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD
Al	557	13	1.1	10	1.5	4	6.6	12	11	11	4.5	10	NA	-
B	237	20	1.6	15	0.6	9	8.1	6	2.9	19	5.4	20	NA	-
Ba	11	9	16	55	27	4	78	53	87	66	78	1	NA	-
Cd	<5	-	>21	65	>20	11	>59	9	>24	10	>11	10	NA	-
Co	8	7	4.8	19	3.6	5	5.8	-	ND	-	15	14	NA	-
Cr	1020	2	0.2	20	0.1	8	3.3	6	2.4	2	5.6	3	NA	-
Cu	<10	-	ND	-	>2	1	>340	6	>260	6	>7	16	NA	-
Fe	207	15	2.9	58	6.1	29	475	11	208	10	1150	5	NA	-
Pb	74	5	3.5	24	3.0	5	21	22	17	49	14	12	NA	-
Mn	68	6	2340	86	1900	-	3470	6	1940	8	6560	3	NA	-
Mo	35600	1	0.9	48	0.5	11	0.8	10	1.2	11	1.1	12	NA	-
Ni	<50	-	>5	59	>6	5	>22	11	>6	26	>66	4	NA	-
Sn	<10	-	>31	17	>24	3	>34	17	>36	14	>45	1	NA	-
Ti	2	-	2.5	10	3.5	7	29	10	ND	-	ND	-	NA	-
V	81	1	1.3	6	0.9	4	28	8	13	10	41	3	NA	-
Y	<5	-	ND	-	ND	-	>21	9	ND	-	>17	13	NA	-
Zn	12	51	129	167	100	12	53000	12	22000	7	78000	1	NA	-
Phen(d)	18	100	0.3	16	0.3	10	0.4	13	NA	-	NA	-	0.6	18
Fluan	13	96	0.4	20	0.3	10	0.4	25	NA	-	NA	-	1.6	22
Pyr	8	96	0.4	22	0.3	10	0.3	10	NA	-	NA	-	2.4	46
Phol	8	18	0.9	57	0.5	35	0.3	60	NA	-	NA	-	0.6	12

(a) Relative to amount found using distilled water.
(b) More complete description of the leaching media are given in Table 6.
(c) Average of three runs; blank value has been subtracted.
(d) Phen - phenanthrene; Fluan - fluoranthene; Pyr - pyrene; Phol - phenol.

NA = Not analyzed.
ND = Not detected.
RSD = Relative standard deviation.

TABLE 11. COMPOSITION OF LEACHATES FROM STILL BOTTOMS

Analyte	Amount Found Using Distilled Water		Relative Amt (RA)[a] Found & Percent Relative Std Dev (RSD) Using Given Leaching Medium[b]											
			EP		0.1M NaOAc, pH 4.0		0.05M NaCit, pH 5.0		0.02M NaCit, pH 5.0		0.05M $Na_2S_2O_4$ + 0.05M NaCit, pH 5.0		0.01% Igepal + 0.05M NaCit, pH 5.0	
	µg/ℓ[c]	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD
Al	2620	19	1.0		1.6	5	5.0	6	6.5	2	4.5	6	NA	-
B	373	11	1.0		1.9	8	2.0	15	2.0	12	1.9	7	NA	-
Ba	1100	3	1.0		0.1	12	1.9	0	1.2	50	0.2	15	NA	-
Co	<50	-	1.0		ND	-	>2	14	>2	3	>2	12	NA	-
Cr	<100	-	1.0		ND	-	>8	5	>8	15	>10	2	NA	-
Cu	174000	11	1.0		1.2	13	1.3	4	1.3	7	1.3	4	NA	-
Fe	249000	11	1.0		1.0	3	1.5	1	1.5	2	1.7	1	NA	-
Pb	<500	-	1.0		ND	-	>2	8	>2	16	>2	0	NA	-
Mn	2690	4	1.0		1.0	3	1.0	1	1.0	5	1.1	3	NA	-
Mo	<100	-	1.0		ND	-	ND	-	ND	-	>1	12	NA	-
Ni	1150	7	1.0		1.0	2	1.4	1	1.5	23	1.5	3	NA	-
Ti	<50	-	1.0		ND	-	>7	4	>7	12	>7	4	NA	-
V	<50	-	1.0		>1	13	>3	12	>2	12	>3	2	NA	-
Zn	3550	10	1.0		1.0	9	1.7	3	1.8	8	3.2	4	NA	-
Hg	<1	-	1.0		ND	-	ND	-	>1	14	>16	31	NA	-
pDCBz[d]	35	15	1.0		NA	-	0.9	14	NA	-	NA	-	1.2	2
BCEE	32	82	1.0		NA	-	ND	-	NA	-	NA	-	1.7	5
oDCB	15	13	1.0		NA	-	0.9	11	NA	-	NA	-	1.2	3
HCEt	58	33	1.0		NA	-	0.9	19	NA	-	NA	-	1.1	8
HCBud	178	88	1.0		NA	-	0.4	15	NA	-	NA	-	0.3	18
TCBz	29	75	1.0		NA	-	0.3	6	NA	-	NA	-	0.5	5
HCBz	<5	-	1.0		NA	-	ND	-	NA	-	NA	-	>1	29
Phen	6	75	1.0		NA	-	0.3	99	NA	-	NA	-	ND	-
Phol	340	10	1.0		NA	-	3.8	75	NA	-	NA	-	0.9	7

(a) Relative to amount found using distilled water.
(b) More complete descriptions of the leaching media are given in Table 6.
(c) Average of three runs; blank value has been subtracted.
(d) pDCBz - 1,4-dichlorobenzene
BCEE - bis(2-chloroethyl)ether
oDCB - 1,2-dichlorobenzene
HCEt - hexachloroethane
HCBud - hexachlorobutadiene
TCBz - 1,2,4-trichlorobenzene
HCBz - hexachlorobenzene
Phen - phenanthrene
Phol - phenol.

NA = Not analyzed.
ND = Not detected.
RSD = Relative standard deviation.

TABLE 12. COMPOSITION OF LEACHATES FROM INK PIGMENT WASTE

Analyte	Amount Found Using Distilled Water		Relative Amt (RA)[(a)] Found & Percent Relative Std Dev (RSD) Using Given Leaching Medium[(b)]											
			EP		0.1M NaOAc, pH 4.0		0.05M NaCit, pH 5.0		0.02M NaCit, pH 5.0		0.05M $Na_2S_2O_4$ + 0.05M NaCit, pH 5.0		0.01% Igepal + 0.05M NaCit, pH 5.0	
	μg/ℓ[(c)]	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD
Al	11300	4	0.3	5	0.4	13	1.4	9	0.5	14	1.4	6	NA	-
B	3790	3	1.0	14	0.8	6	1.1	11	0.8	14	1.0	7	NA	-
Ba	573	8	4.3	5	3.6	8	6.0	34	2.4	5	0.2	21	NA	-
Cd	<5	-	>3	3	>2	13	>2	5	ND	-	ND	-	NA	-
Co	<5	-	>5	9	>3	11	>4	7	ND	-	ND	-	NA	-
Cr	1050	4	0.5	7	0.7	2	1.2	16	0.8	8	1.3	4	NA	-
Cu	383	7	0.1	15	0.1	14	0.1	26	ND	-	ND	-	NA	-
Fe	3910	14	0.3	35	0.3	14	1.8	15	0.5	12	2.1	-	NA	-
Pb	5690	5	0.6	20	0.8	19	1.3	16	0.4	29	1.0	4	NA	-
Mn	110	10	7.6	7	10	21	11	22	1.6	23	11	11	NA	-
Mo	487	2	0.3	8	0.4	20	0.9	4	0.8	5	0.9	6	NA	-
Ni	<50	-	>2	8	>1	20	>1	8	ND	-	ND	-	NA	-
Sn	46	10	3.9	3	2.1	10	2.5	1	ND	-	ND	-	NA	-
Ti	85	17	0.3	6	0.3	10	1.0	18	ND	-	ND	-	NA	-
V	10	22	3.0	9	1.8	22	3.3	8	ND	-	ND	-	NA	-
Zn	110	27	14	15	13	8	1.4	37	6.5	2	7.3	6	NA	-
pDCBz[(d)]	310	3	0.7	46	0.6	8	0.8	3	NA	-	NA	-	0.7	21
oDCBz	550	3	0.7	47	0.7	8	0.8	3	NA	-	NA	-	0.7	17
Naph	810	7	0.6	28	0.7	5	0.8	2	NA	-	NA	-	0.7	23
Acny	100	32	0.7	25	0.5	10	0.9	7	NA	-	NA	-	0.6	48
Acne	56	27	0.9	29	0.5	15	0.9	2	NA	-	NA	-	0.6	47
Fluo	110	22	0.7	25	1.1	22	2.1	6	NA	-	NA	-	1.3	67
Phen	290	28	1.0	24	2.6	26	5.9	6	NA	-	NA	-	1.4	82
Fluan	88	20	1.3	24	2.8	31	7.2	3	NA	-	NA	-	0.6	68
Pyr	76	28	1.0	23	2.5	31	7.5	4	NA	-	NA	-	0.6	35
BEHP	620	14	0.7	8	0.5	31	0.9	4	NA	-	NA	-	0.8	33
Chry	49	45	1.0	41	0.4	62	7.3	33	NA	-	NA	-	0.8	42
DOPh	92	9	1.0	28	0.4	31	0.9	5	NA	-	NA	-	0.7	32
BbkF	32	44	2.2	14	0.2	67	11	13	NA	-	NA	-	3.4	150
Phol	2100	9	0.9	27	2.1	58	1.0	5	NA	-	NA	-	1.0	6
PCP	96	59	0.5	29	ND	-	1.3	13	NA	-	NA	-	1.0	29

(a) Relative to amount found using distilled water.

(b) More complete descriptions of the leaching media are given in Table 6.

(c) Average of three runs; blank value has been subtracted.

(d) pDCBz - 1,4-dichlorobenzene
oDCBz - 1,2-dichlorobenzene
Naph - naphthalene
Acny - acenaphythylene
Acne - acenaphthene
Fluo - fluorene
Phen - phenanthrene
Fluan - fluoranthene
Pry - pyrene
BEHP - bis(2-ethylhexyl)phthalate
Chry - chrysene
DOPh - dioctyl phthalate
BbkF - benzo(b &/or k)fluoranthene
Phol - phenol
PCP - pentachlorophenol.

NA = Not analyzed.
ND = Not detected.
RSD = Relative standard deviation.

TABLE 13. COMPOSITION OF LEACHATES FROM PHARMACEUTICAL WASTE

Analyte	Amount Found Using Distilled Water		Relative Amt (RA)(a) Found & Percent Relative Std Dev (RSD) Using Given Leaching Medium(b)											
			EP		0.1M NaOAc, pH 4.0		0.05M NaCit, pH 5.0		0.02M NaCit, pH 5.0		0.05M $Na_2S_2O_4$ + 0.05M NaCit, pH 5.0		0.01% Igepal + 0.05M NaCit, pH 5.0	
	µg/ℓ(c)	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD
Al	<40	-	ND	-	>5	19	>15	3	>10	16	>12	13	NA	-
B	209	6	0.4	7	0.4	51	3.6	13	0.8	34	0.4	6	NA	-
Ba	785	1	0.1	3	ND	-	0.8	71	1.0	78	0.2	9	NA	-
Cu	27	25	0.2	5	ND	-	ND	-	1.6	89	9.6	6	NA	-
Fe	72	14	1.4	11	2.2	37	46	32	28	34	33	5	NA	-
Mn	20	3	13	1	24	7	37	30	25	5	24	7	NA	-
Zn	809	5	<0.1	23	0.3	47	2.4	13	1.4	35	0.9	3	NA	-
Phol(d)	410	130	0.5	23	NA	-	0.6	3	NA	-	NA	-	0.5	9

(a) Relative to amount found using distilled water.
(b) More complete descriptions of the leaching media are given in Table 6.
(c) Average of three runs; blank value has been subtracted.
(d) Phol = phenol.

NA = Not analyzed.
ND = Not detected.
RSD = Relative standard deviation.

TABLE 14. COMPOSITION OF LEACHATES FROM COAL GASIFICATION COAL TAR WASTE

	Amount Found Using Distilled Water		Relative Amount (RA)[(a)] Found & Percent Relative Std Dev (RSD) Using Given Leaching Medium[(b)]											
			EP		0.1M NaOAc, pH 4.0		0.05M NaCit, pH 5.0		0.02M NaCit, pH 5.0		0.05M $Na_2S_2O_4$ + 0.05M NaCit, pH 5.0		0.01% Igepal + 0.05M NaCit, pH 5.0	
Analyte[(d)]	μg/ℓ[(c)]	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD	RA	RSD
Naph	2,100	5	0.8	2	NA	-	0.3	16	NA	-	NA	-	0.9	9
Acne	970	10	0.7	5	NA	-	0.1	21	NA	-	NA	-	0.7	8
Fluo	570	49	0.4	6	NA	-	<0.1	22	NA	-	NA	-	0.4	14
Phen	930	22	0.3	11	NA	-	<0.1	22	NA	-	NA	-	0.3	31
Fluan	270	32	0.3	23	NA	-	<0.1	20	NA	-	NA	-	0.3	31
Pry	210	25	0.3	24	NA	-	<0.1	35	NA	-	NA	-	0.3	60
Chry	160	75	0.2	26	NA	-	ND	-	NA	-	NA	-	0.2	70
BbkF	130	44	0.3	32	NA	-	ND	-	NA	-	NA	-	0.3	67
Phol	12,000	25	1.0	38	NA	-	0.3	6	NA	-	NA	-	0.5	47
DMP	5,200	29	0.8	5	NA	-	0.2	7	NA	-	NA	-	1.1	9

NA = Not analyzed.
ND = Not detected.
RSD = Relative standard deviation.

(a) Relative to amount found using distilled water.
(b) More complete descriptions of the leaching media are given in Table 6.
(c) Average of three runs; blank value has been subtracted.
(d) Naph - naphthalene
Acne - acenaphthene
Fluo - fluorene
Phen - phenanthrene
Fluan - fluoranthene
Pyr - pyrene
Chry - chrysens
BbkF - benzo(b &/or k)fluoranthene
Phol - phenol
DMP - 2,4-dimethylphenol.

The data in Table 11 for metals again illustrate the greater leaching ability of citrate relative to either distilled water or acetate buffer. However, the effect of citrate was not as pronounced for the still bottom sample as it was for the baghouse dust sample. The addition of hydrosulfite to the citrate buffer had no significant effect on the mobility of metals in the still bottoms sample. The 0.02 M and 0.05 M citrate buffers gave virtually identical levels for metals in the still bottom sample.

The data for the ink pigment sample are shown in Table 12. High levels of many organic priority pollutants and metals were observed in the leachates from this sample. For organics other than PNAs, the leaching medium composition had very little effect. Benzo(k)fluoranthene was present at a higher level in the citrate medium, both with and without Igepal added. However, several other PNAs (fluoranthene, phenanthrene, fluorene, pyrene, and chrysene) were elevated in the citrate medium alone but not in the Igepal/citrate medium. This result indicates that the differences observed are not significant and probably could not be reproduced. Lower molecular weight PNAs (naphthalene, acenaphthene, and acenaphthalene) were present at comparable levels in all leaching media.

The data in Table 12 for metals reveal that the EP and 0.1 M acetate buffer, pH 4, gave comparable results for all metals. The levels of several metals (Al, Cu, Cr, Fe, Pb, and Mo) were lower in the EP than in distilled water, while several other metals (Ba, Cd, Co, Mn, Sn, V, and Zn) were high in the EP. Citrate does not give significantly higher levels of any of the metals relative to acetate or the EP. The addition of hydrosulfite did not significantly affect the leachate content. Since this waste was highly alkaline, the distilled water leachate actually represents an alkaline leaching condition, which may help to explain the results obtained for certain metals.

The data obtained for pharmaceutical waste are presented in Table 13. Only one priority pollutant organic compound, phenol, was found in the leachate of this waste. The level of phenol was highest in the distilled water leachate with all of the other leachates, including the EP, containing approximately 50 percent of the amount found in distilled water. Significant levels of Al, B, Ba, Cu, Fe, Mn, and Zn were found in the pharmaceutical waste leachates (Al was not found in the distilled water leachate). Al, Mn, and Fe were elevated, relative to distilled water, in all the leachates except the EP in which only Mn was significantly elevated. Acetate buffer gave slightly higher metal levels than the EP and citrate gave greatly increased levels of Al and Fe. The effect of added hydrosulfite was negligible except that a lower level of B and a higher level of Cu were obtained relative to 0.05 M citrate alone.

The data for coal gasification tar are presented in Table 14. These leachates were analyzed for organics but not for metals because of relatively high organic content of the material. In general, distilled water gave higher levels of the organic components present (PNAs and phenol) than any of the other media. Organic levels in the EP were approximately 2 to 5 times less than for distilled water, and 0.05 M citrate contained substantially lower levels than the EP. The addition of Igepal to 0.05 M citrate increased the level of organics leached somewhat, but lower levels than distilled water were still observed.

Representative reconstructed gas chromatograms for both volatile and semivolatile organic analysis reported in Tables 9-14 for the five samples are presented in Figures 2 to 10 (volatiles were not determined in the baghouse dust samples).

The diverse nature of the wastes studied and the relatively limited current understanding of the parameters affecting mobility of chemical constituents in solid wastes makes it difficult to summarize the results in such a way that predictions can be made as to what results to anticipate in other experimental situations. However, several relatively concise statements can be made concerning the overall results obtained in this task:

(1) The effect of leaching medium composition on organic mobility is slight whereas the effect on metal mobility is frequently very large.

(2) The EP and 0.1 M acetate buffer, pH 4, gave comparable results for both organics and metals in all of the wastes studied.

(3) While the addition of citrate generally increases the mobility of metals, the increase relative to distilled water, can vary from negligible to 10^5 times.

(4) The addition of hydrosulfite does not generally affect the mobility of metals to a significant extent.

(5) The addition of surfactant does not generally affect the mobility of organics to a significant extent.

(6) The total amount of metals leached from a given quantity of waste using citrate is dependent upon the citrate concentration, with high concentration of citrate leaching more metals.

INTERLABORATORY COMPARISON STUDY (TASK 6)

Battelle and SoRI conducted an interlaboratory comparison of the potential mobility and total content methods using the ink pigment and still bottoms wastes. In order to ensure that sample inhomogeneity was minimized, the wastes were remixed at Battelle and ten 75-g samples and a 200-g sample were prepared for each laboratory. The leachates from five of the 75-g samples were used for metal analysis and the leachates from the remaining five 75-g samples were used for organic determinations. The 200-g sample was used for total content analyses. These samples were shipped and stored at 0° to 5°C until use.

It was decided that both laboratories would use the same source of organic standards for spiking experiments to eliminate any analytical variabilities due to differences in compound purity. The standards used for spiking

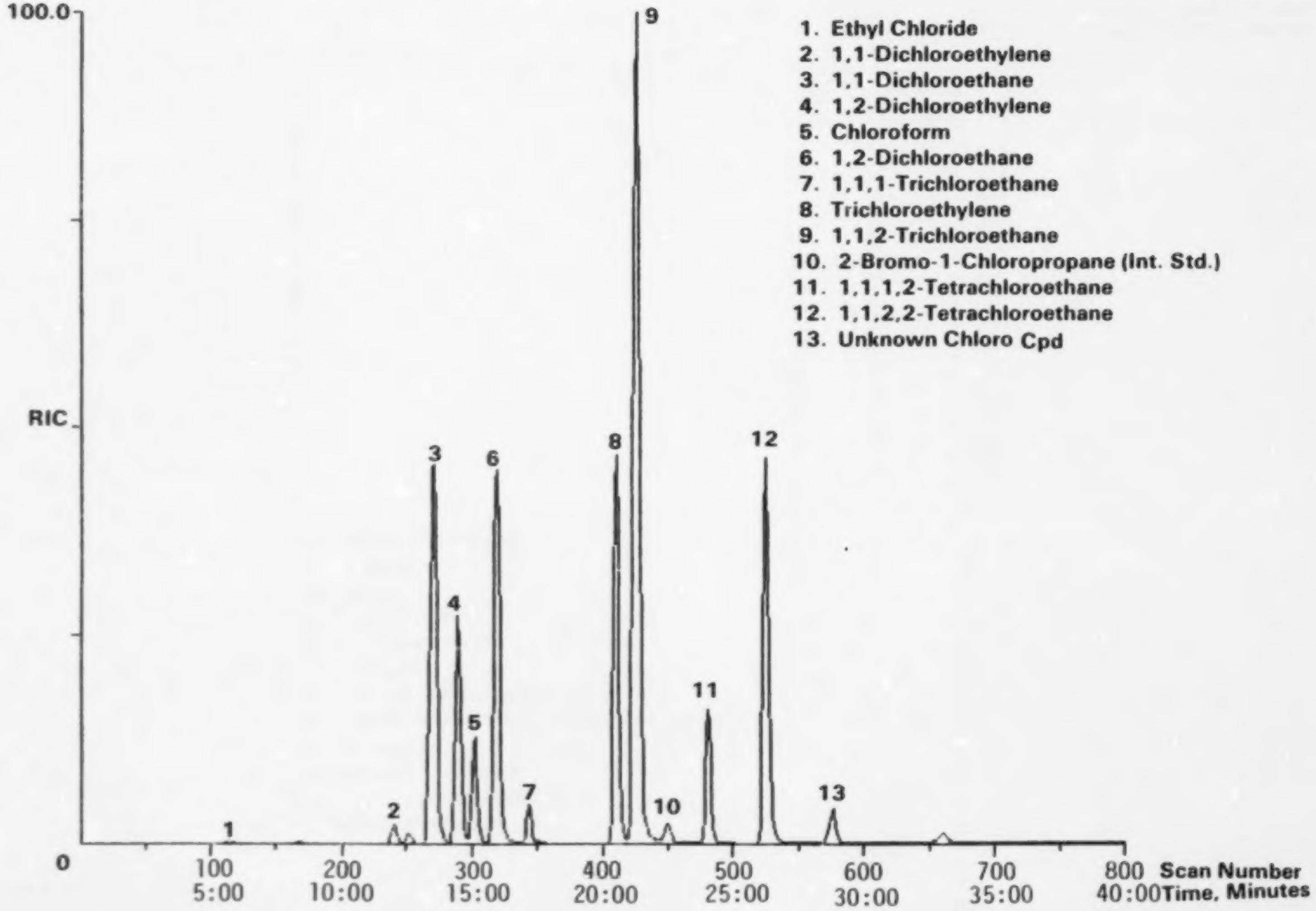


FIGURE 2. RECONSTRUCTED GAS CHROMATOGRAM FOR VOLATILE ORGANICS IN STILL BOTTOMS LEACHATE

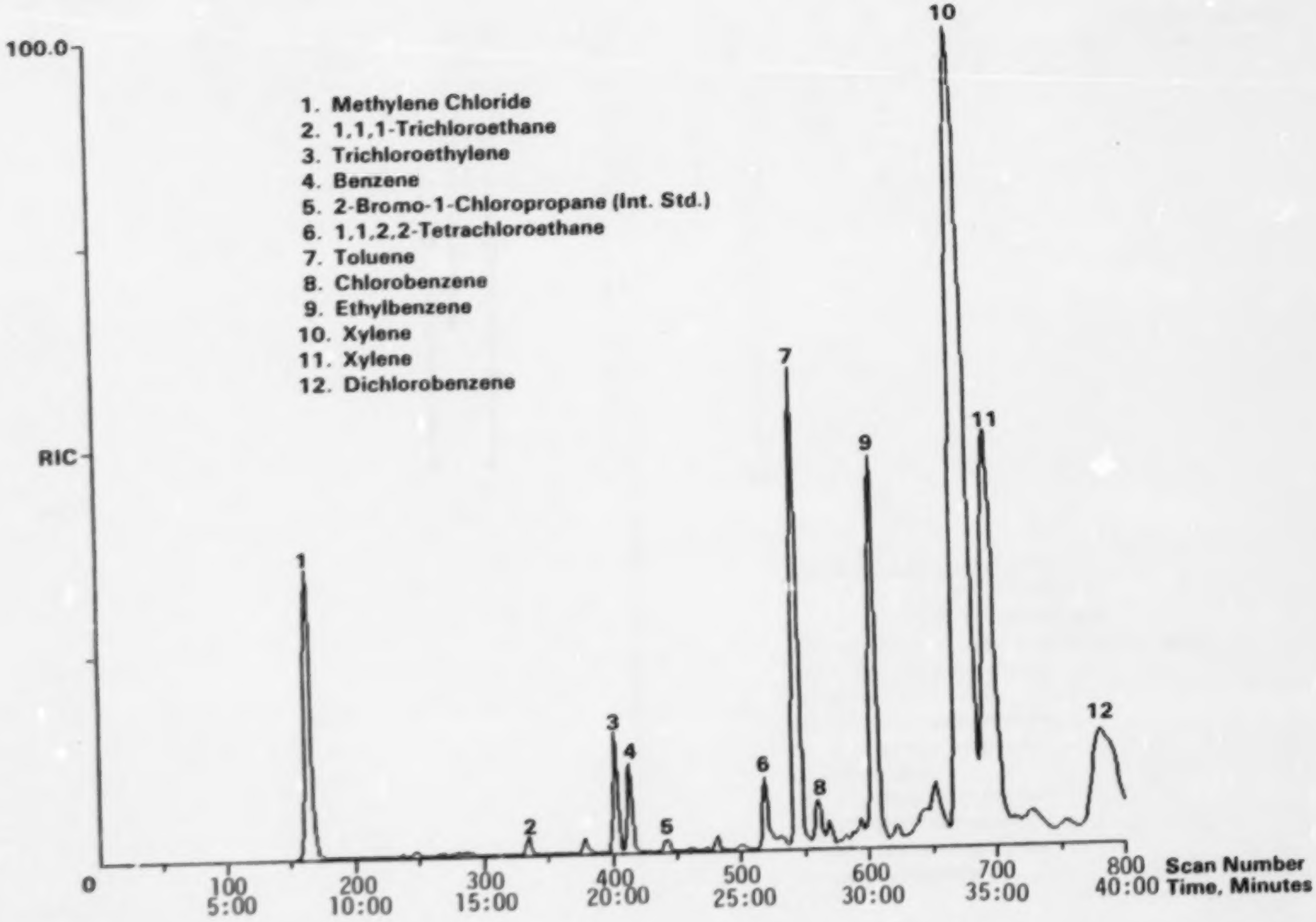
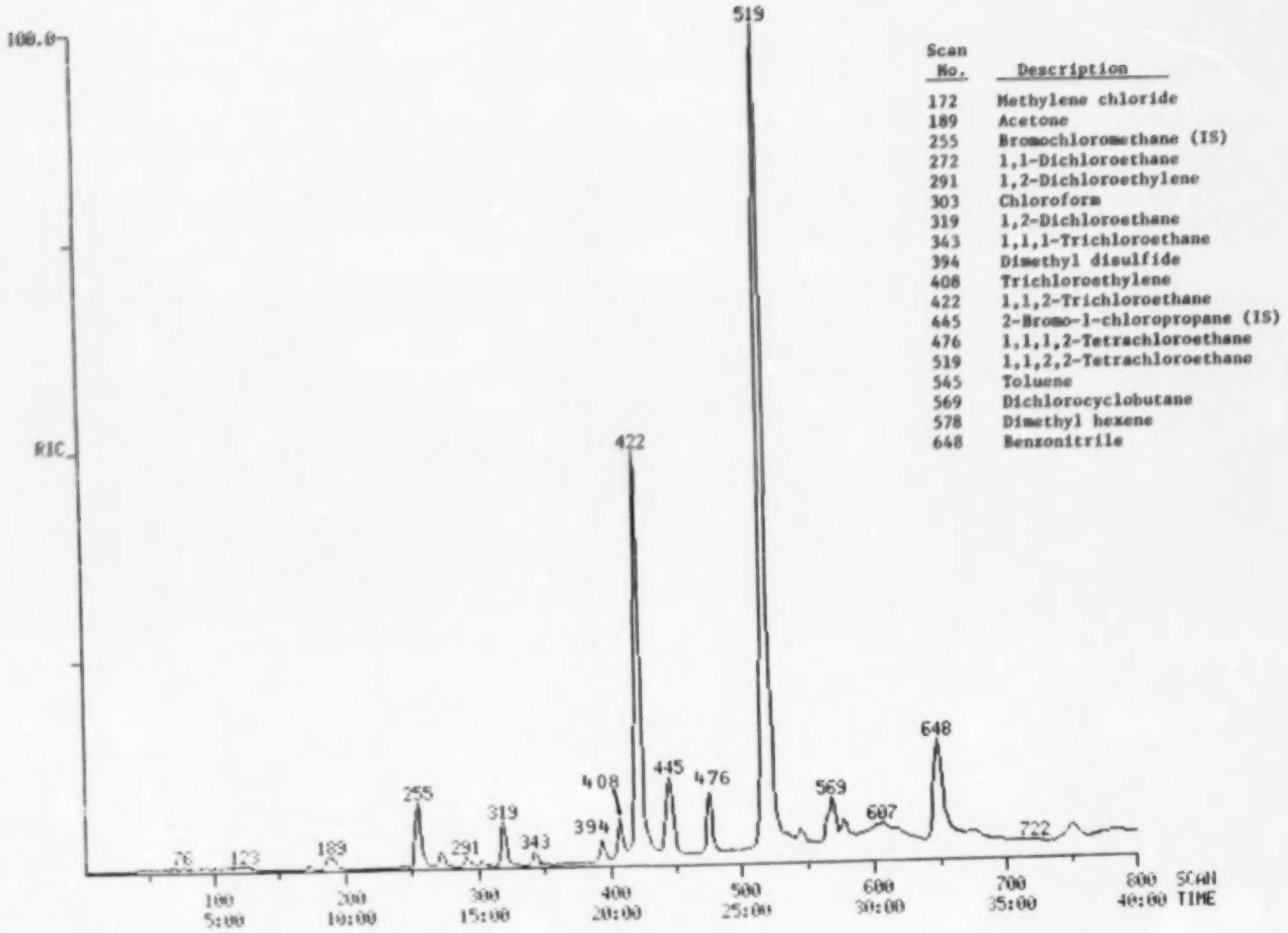
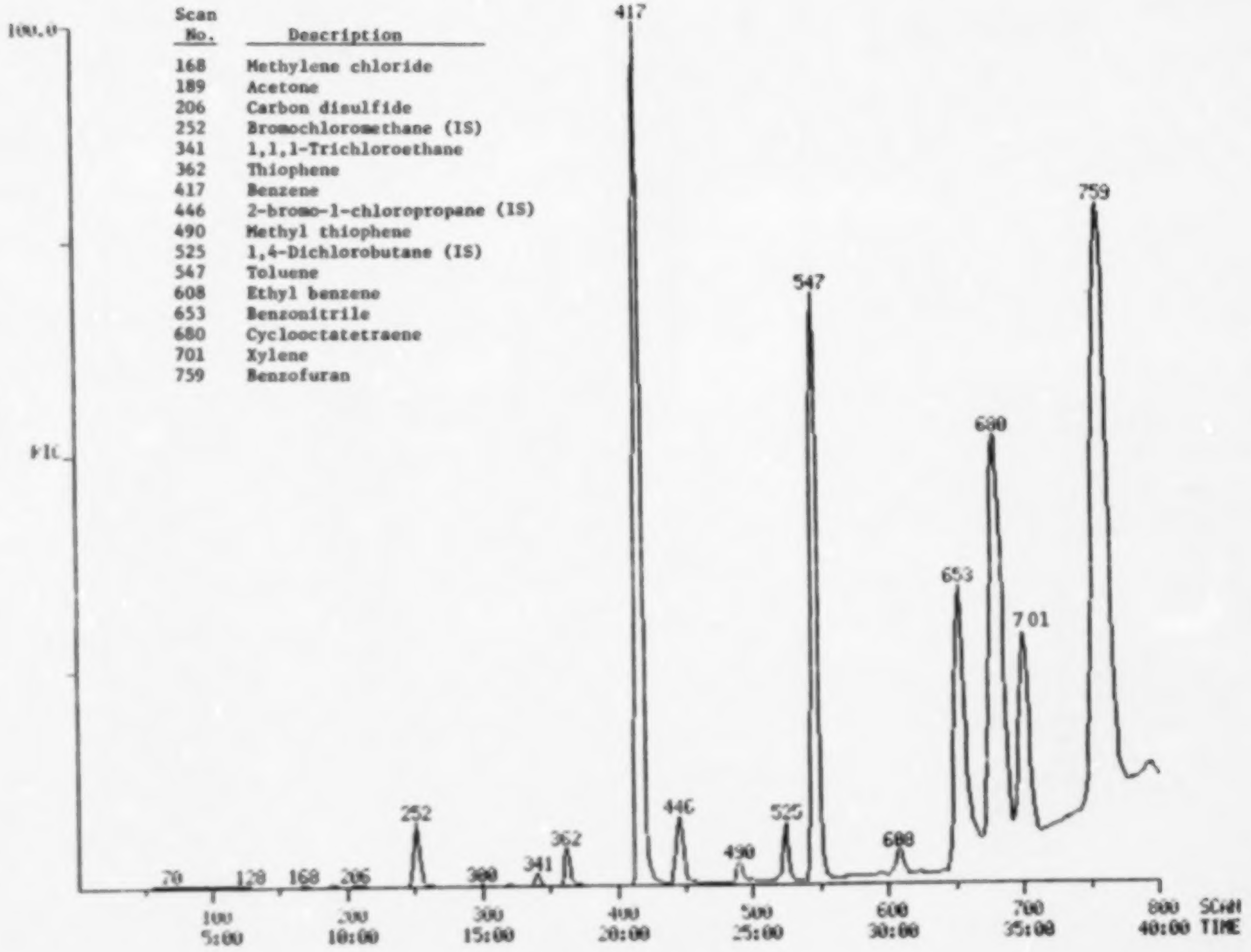


FIGURE 3. RECONSTRUCTED GAS CHROMATOGRAM FOR VOLATILE ORGANICS IN INK PIGMENT LEACHATE



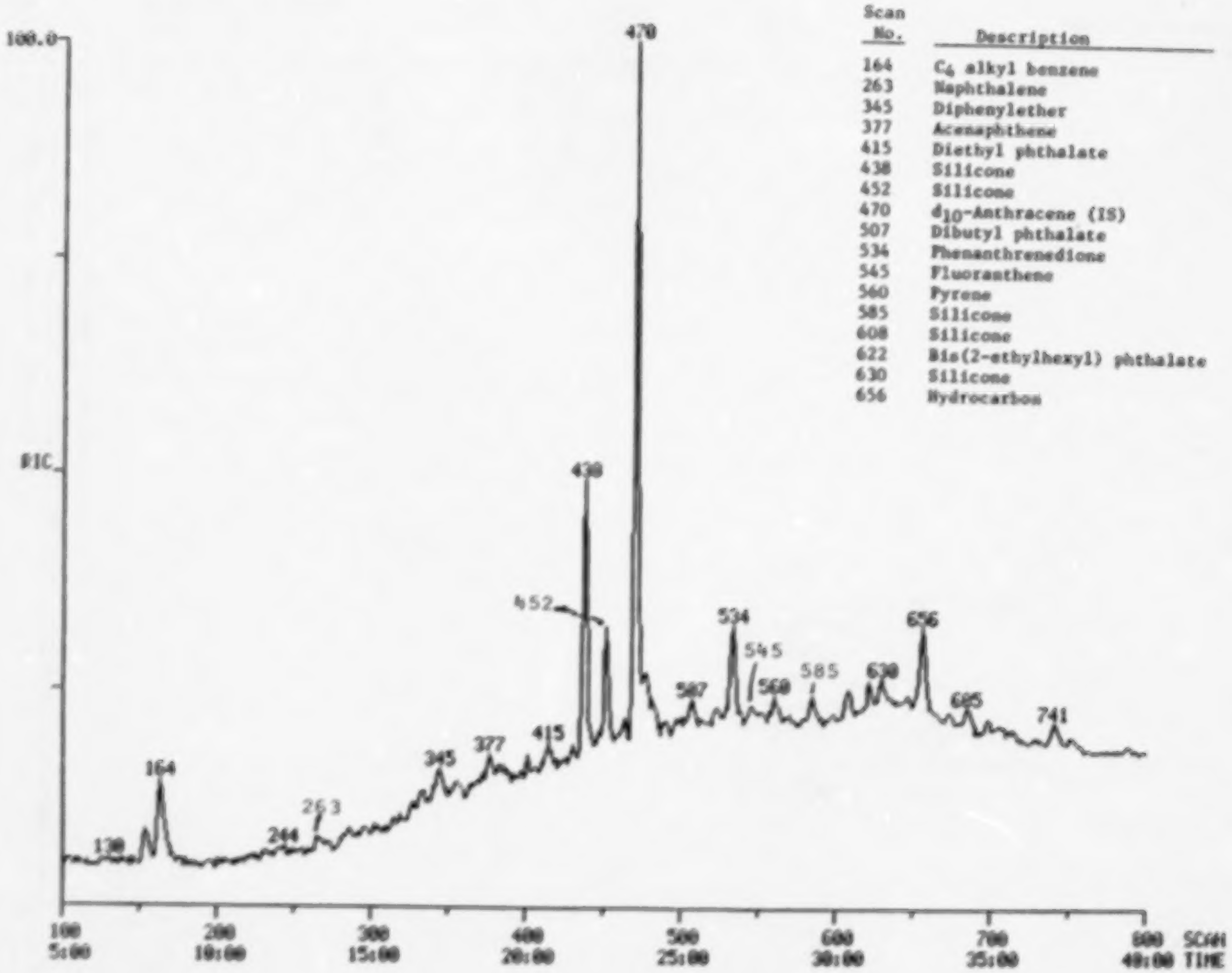
Scan No.	Description
172	Methylene chloride
189	Acetone
255	Bromochloromethane (IS)
272	1,1-Dichloroethane
291	1,2-Dichloroethylene
303	Chloroform
319	1,2-Dichloroethane
343	1,1,1-Trichloroethane
394	Dimethyl disulfide
408	Trichloroethylene
422	1,1,2-Trichloroethane
445	2-Bromo-1-chloropropane (IS)
476	1,1,1,2-Tetrachloroethane
519	1,1,2,2-Tetrachloroethane
545	Toluene
569	Dichlorocyclobutane
578	Dimethyl hexene
648	Benzonitrile

FIGURE 4. RECONSTRUCTED GAS CHROMATOGRAM FOR VOLATILE ORGANICS IN PHARMACEUTICAL WASTE LEACHATE



Scan No.	Description
168	Methylene chloride
189	Acetone
206	Carbon disulfide
252	Bromochloromethane (IS)
341	1,1,1-Trichloroethane
362	Thiophene
417	Benzene
446	2-bromo-1-chloropropane (IS)
490	Methyl thiophene
525	1,4-Dichlorobutane (IS)
547	Toluene
608	Ethyl benzene
653	Benzonitrile
680	Cyclooctatetraene
701	Xylene
759	Benzofuran

FIGURE 5. RECONSTRUCTED GAS CHROMATOGRAM FOR VOLATILE ORGANICS IN COAL GASIFICATION TAR LEACHATE



Scan No.	Description
164	C_4 alkyl benzene
263	Naphthalene
345	Diphenylether
377	Acenaphthene
415	Diethyl phthalate
438	Silicone
452	Silicone
470	d_{10}-Anthracene (IS)
507	Dibutyl phthalate
534	Phenanthrenedione
545	Fluoranthene
560	Pyrene
585	Silicone
608	Silicone
622	Bis(2-ethylhexyl) phthalate
630	Silicone
656	Hydrocarbon

FIGURE 6. RECONSTRUCTED GAS CHROMATOGRAM FOR SEMIVOLATILE ORGANICS IN BAGHOUSE DUST LEACHATE

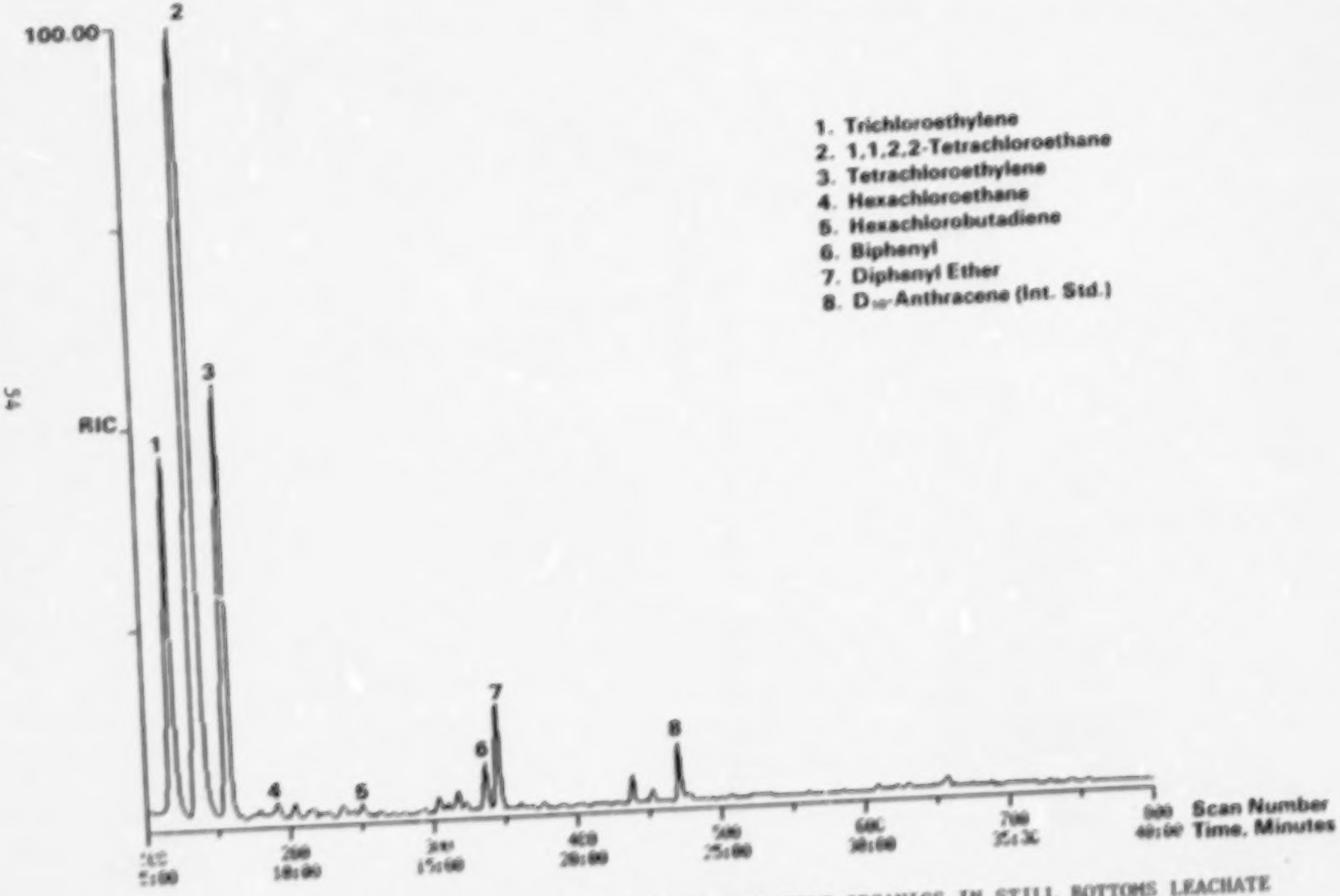


FIGURE 7. RECONSTRUCTED GAS CHROMATOGRAM FOR SEMIVOLATILE ORGANICS IN STILL BOTTOMS LEACHATE

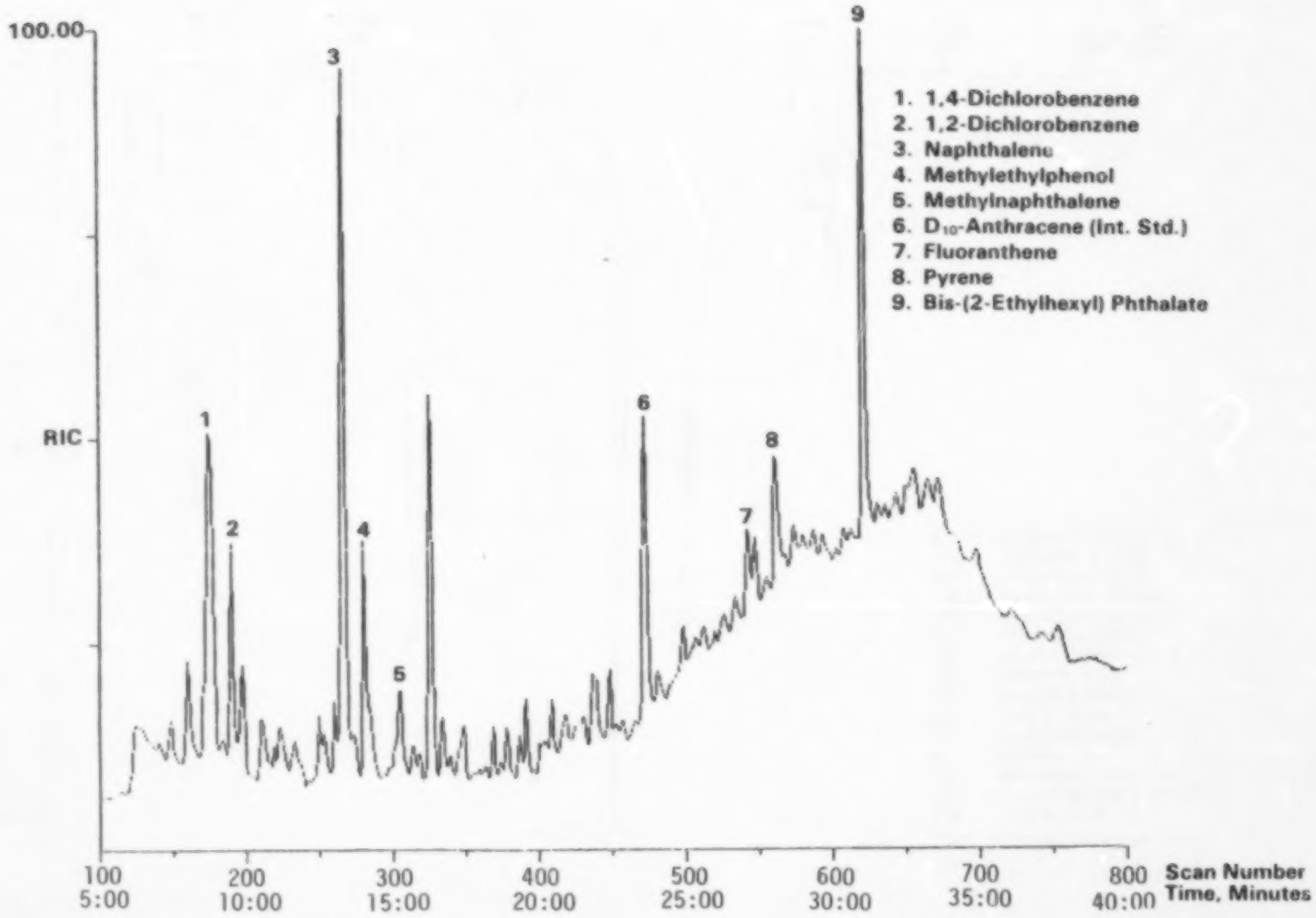
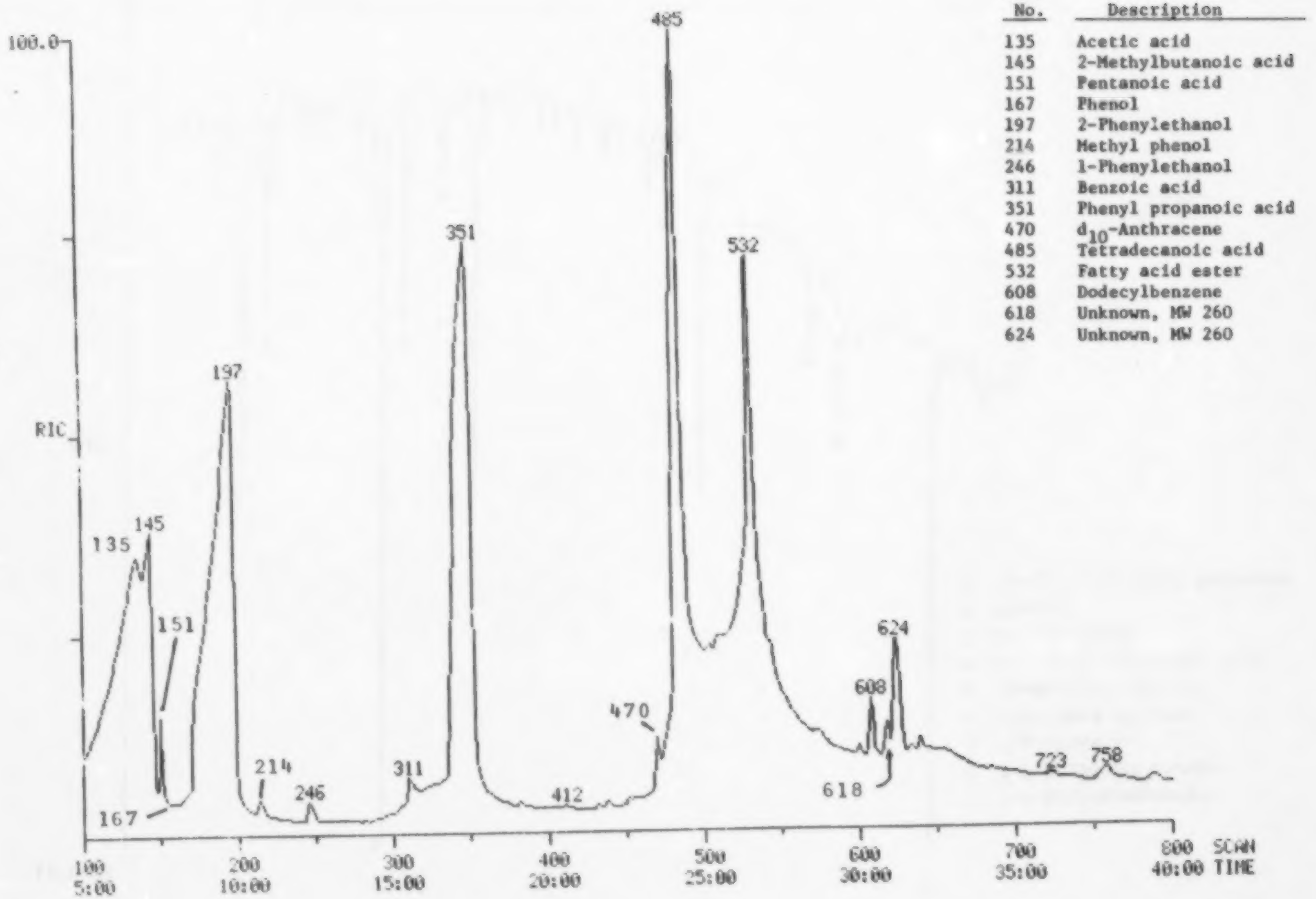
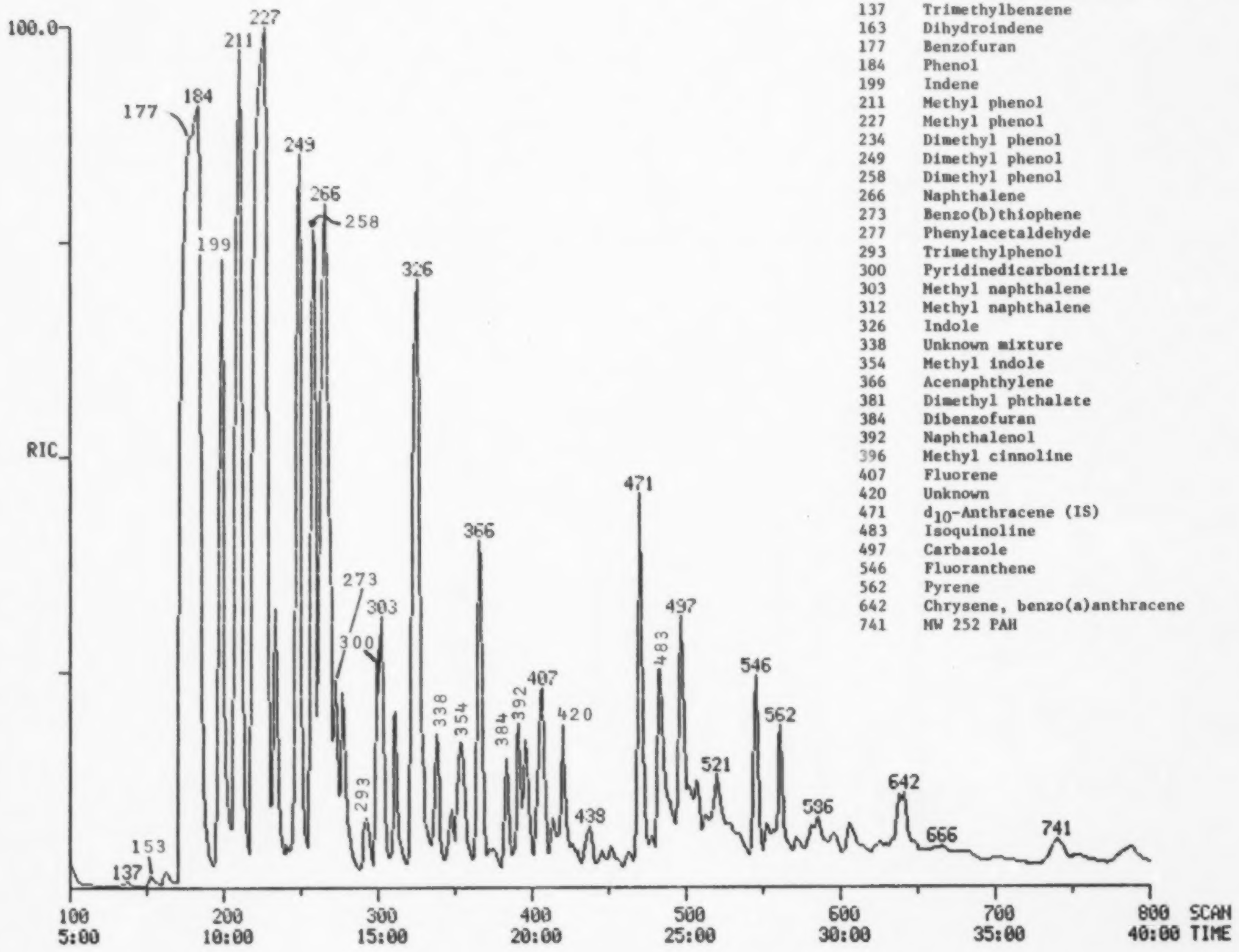


FIGURE 8. RECONSTRUCTED GAS CHROMATOGRAM FOR SEMIVOLATILE ORGANICS IN INK PIGMENT LEACHATE



Scan No.	Description
135	Acetic acid
145	2-Methylbutanoic acid
151	Pentanoic acid
167	Phenol
197	2-Phenylethanol
214	Methyl phenol
246	1-Phenylethanol
311	Benzoic acid
351	Phenyl propanoic acid
470	d_{10}-Anthracene
485	Tetradecanoic acid
532	Fatty acid ester
608	Dodecylbenzene
618	Unknown, MW 260
624	Unknown, MW 260

FIGURE 9. RECONSTRUCTED GAS CHROMATOGRAM FOR SEMIVOLATILE ORGANICS IN PHARMACEUTICAL WASTE LEACHATE



Scan No.	Description
137	Trimethylbenzene
163	Dihydroindene
177	Benzofuran
184	Phenol
199	Indene
211	Methyl phenol
227	Methyl phenol
234	Dimethyl phenol
249	Dimethyl phenol
258	Dimethyl phenol
266	Naphthalene
273	Benzo(b)thiophene
277	Phenylacetaldehyde
293	Trimethylphenol
300	Pyridinedicarbonitrile
303	Methyl naphthalene
312	Methyl naphthalene
326	Indole
338	Unknown mixture
354	Methyl indole
366	Acenaphthylene
381	Dimethyl phthalate
384	Dibenzofuran
392	Naphthalenol
396	Methyl cinnoline
407	Fluorene
420	Unknown
471	d_{10}-Anthracene (IS)
483	Isoquinoline
497	Carbazole
546	Fluoranthene
562	Pyrene
642	Chrysene, benzo(a)anthracene
741	MW 252 PAH

FIGURE 10. RECONSTRUCTED GAS CHROMATOGRAM FOR SEMIVOLATILE ORGANICS IN COAL TAR LEACHATE

TABLE 15. COMPOSITION OF STANDARD SOLUTION A

Compound	Concentration, µg/ml (a)
1. N-Nitrosodimethylamine	250
2. N-Nitrosodipropylamine	50
3. Nitrobenzene	50
4. Isophorone	250
5. Acenaphthylene	50
6. Dimethyl phthalate	50
7. 2,6-Dinitrotoluene	50
8. Fluorene	250
9. 2,4-Dinitrotoluene	250
10. Diethyl phthalate	250
11. Dibutyl phthalate	50
12. Fluoranthene	250
13. Pyrene	50
14. Chrysene	250
15. Dioctyl phthalate	250
16. Benzo(k)fluoranthene	50

(a) In 1:1 methanol:2-propanol.

TABLE 16. COMPOSITION OF STANDARD SOLUTION B

Compound	Concentration, μg/ml(a)
1. 1,4-Dichlorobenzene	500
2. Bis(2-chloroethyl)ether	100
3. 1,2-Dichlorobenzene	100
4. Bis(2-chloroisopropyl)ether	500
5. Hexachlorobutadiene	500
6. 1,2,4-Trichlorobenzene	100
7. Hexachlorocyclopentadiene	100
8. 4-Chlorophenyl phenyl ether	100
9. Hexachlorobenzene	500
10. 4-Bromophenyl phenyl ether	500
11. 4,4'-DDE	500
12. Endrin	500
13. 2,4,2',4'-Tetrachlorobiphenyl	500
14. 2,4,6,2',4',6'-Hexachlorobiphenyl	100
15. g-BHC (lindane)	100
16. 4,4'-DDD	100

(a) In methanol.

TABLE 17. COMPOSITION OF STANDARD SOLUTION C

Compound	Concentration, μg/ml(a)
1. Benzidine	100
2. 3,3'-Dichlorobenzidine	500
3. Phenol	1000
4. 2,4-Dimethylphenol	100
5. 2-Chlorophenol	500
6. 2,4-Dichlorophenol	100
7. 2,4-Dinitrophenol	500
8. 4-Nitrophenol	100
9. 2,4,6-Trichlorophenol	500
10. Pentachlorophenol	100

(a) In methanol.

TABLE 18. COMPOSITION OF STANDARD SOLUTION D

Compound	Concentration, μg/ml(a)
1. Methylene chloride	50
2. 1,1-Dichloroethene	10
3. 1,1-Dichloroethane	10
4. trans-1,2-Dichloroethene	50
5. Chloroform	10
6. 1,2-Dichloroethane	50
7. 1,1,1-Trichloroethane	10
8. Carbon tetrachloride	50
9. Trichloroethene	50
10. Benzene	50
11. 1,1,2-Trichloroethane	10
12. 1,1,2,2-Tetrachloroethane	10
13. Tetrachloroethene	50
14. Toluene	50
15. Chlorobenzene	50
16. Ethylbenzene	50

(a) In methanol.

leachates for organic analysis were prepared as four separate spiking solutions by Battelle and shipped in ampules to SoRI. The concentration of compounds used for each of the four solutions, designated as Solutions A, B, C, and D, is shown in Tables 15-18. For the semivolatile organics analyses, 600 µl of Solution A, 300 µl of Solution B, and 300 µl of Solution C were used to spike 300 ml of leachate. Solution D was used to spike the leachates for volatile organic analysis, 2 µl for 40 ml of leachate from still bottoms and 200 µl for 40 ml of leachate from ink pigment.

The standards used for spiking samples for total semivolatiles organic content analysis were prepared as five separate solutions by SoRI and shipped in ampules to Battelle. The concentrations of compounds in these solutions are given in Table 19. Different mixtures of the solutions were used to spike ink pigment and still bottoms based on the total content of the wastes measured by SoRI.

Each of the ten 75-g samples of ink pigment waste and still bottoms was leached using the Solid Waste Leaching Procedure with 0.1M sodium acetate, pH 4 buffer, as the leaching medium. The buffered medium was selected instead of the EP medium or distilled water to minimize differences due to anomalous pH behavior.

Both laboratories rigidly followed the same analysis scheme regarding amount of sample and size of aliquots used for each analysis. The leachates generated for inorganic analysis were divided following final filtration to give three 30-ml aliquots. One of the aliquots was analyzed without spiking; one was spiked at low levels; and one was spiked at high levels.

The leachates targeted for organic analyses were divided following centrifugation but prior to filtration. Two 40-ml aliquots were placed in glass vials for volatile organic analysis; one of these aliquots was analyzed without spiking and one was analyzed with spiking. The remaining leachate was filtered and two 300-ml aliquots were collected for spiked and unspiked semivolatile organic analysis.

Leachate Analyses

The analysis of replicate leachates for metals was conducted by flame and/or flameless AAS and ICAP at Battelle and AAS at SoRI. The intralaboratory precision may be assessed by examining the percent relative standard deviation (RSD) obtained for the five replicates. The data obtained by Battelle using ICAP are presented in Table 20. The RSDs generally were in the 5 percent range with approximately one third of the values in the 20 to 40 percent range. Comparable quantitative results were obtained by Battelle for AA and ICAP as shown in Table 21, however, the levels of these metals were frequently below the detection limit. The recovery of metals spiked into the leachates of ink pigment and still bottoms was excellent (Table 22). The average percent recovery for analysis by AA and ICAP was 102 and 96, respectively. A comparison of BCL and SoRI metals data by AAS for both total content and leachates is given in Table 23. The interlaboratory agreement is considered very good.

TABLE 19. COMPOSITION OF STANDARD SOLUTIONS USED FOR SPIKING IN TOTAL SEMIVOLATILE ORGANIC CONTENT ANALYSIS

Compound	Concentration, mg/ml, in Given Solution					
	K	H	G	I	A-So	J
1,3-Dichlorobenzene			0.166			0.854
1,4-Dichlorobenzene			1.625		0.877	1.096
1,2-Dichlorobenzene			0.429		1.504	1.002
Hexachloroethane						1.002
Bis(2-chloroethyl)ether						1.000
Bis(2-chloroisopropyl)ether				2.00		
Hexachlorobutadiene			14.35			1.023
Nitrobenzene				2.01	0.802	
Naphthalene			0.136		3.010	1.001
1,2,4-Trichlorobenzene			1.034			1.100
Bis(2-chloroethoxy)methane				2.02	0.605	
N-nitrosodi-n-propylamine				2.00		
Hexachlorocyclopentadiene						1.012
2-Chloronaphthalene						0.960
Isophorone				2.02		
Acenaphthylene					2.015	1.008
Acenaphthene			20.10		1.510	1.006
Dimethyl Phthalate					0.503	1.007
2,6-Dinitrotoluene				2.01		
Fluorene					1.004	1.004
2,4-Dinitrotoluene				2.03	1.016	
1,2-Diphenylhydrazine				2.00		
4-Chlorophenyl Phenyl Ether			0.553			1.004
Diethyl Phthalate						1.109
N-Nitrosodiphenylamine						1.000
Hexachlorobenzene						0.807
4-Bromophenyl Phenyl Ether						1.033
Phenanthrene					1.522	1.014
Di-n-butyl Phthalate						1.005
Fluoranthene					2.048	1.004
Pyrene					2.119	1.009
Benzidine				2.01		
Butylbenzyl Phthalate						1.009
Bis(2-ethylhexyl) Phthalate			0.184		3.022	1.006
Benzo(a)anthracene	1.01					0.010
3,3'-Dichlorobenzene				2.01		
Di-n-octyl Phthalate						1.013
Benzo(b)fluoranthene/	1.07					0.011
Benzo(k)fluoranthene	1.12					0.010
Benzo(a)pyrene	1.03					0.010
Benzo(ghi)perylene	1.00					0.011
Dibenzo(ah)anthracene						0.010
Indeno(1,2,3-cd)pyrene						0.005
2-Chlorophenol		10.03			0.407	
2-Nitrophenol		10.05				
Phenol		10.00	0.263		2.425	
2,4-Dimethylphenol		10.04			0.426	
2,4-Dichlorophenol		10.11				
2,4,6-Trichlorophenol		10.06				
4-Chloro-3-methylphenol		10.02				
2,4-Dinitrophenol		10.00				
4,6-Dinitro-o-cresol		10.04				
Pentachlorophenol		10.02			1.520	
4-Nitrophenol		10.02			1.207	
Anthracene					2.208	1.004

TABLE 20. ICAP ANALYSIS OF LEACHATES FOR SOLID WASTES (BATTELLE)

Element	Amount Found for Ink Pigment(a) µg/ℓ	RSD	Amount Found for Still Bottoms(a) µg/ℓ	RSD
Al	5,720	5.8	< 200	--
B	4,080	1.9	< 100	--
Ba	1,810	5.8	1,640	13
Be	< 1	--	< 5	--
Ca	29,500	6.9	130,000	7.6
Co	14	21	< 25	--
Fe	1,550	7.1	50,500	0.4
Mg	227,000	1.4	9,420	5.4
Mn	1,100	5.9	2,570	5.3
Mo	406	4.2	< 50	--
Sn	< 30	--	< 150	--
Ti	75	28	< 25	--
V	< 5	--	< 25	--
Y	< 5	--	< 25	--
Se	< 150	--	< 750	--
Tl	< 400	--	< 2,000	--
Ag	< 10	--	< 50	--
As	< 100	--	< 500	--
Sb	< 100	--	< 500	--
Cd	< 5	--	< 25	--
Cr	710	5.3	<50	--
Cu	52	44	13,300	41
Pb	5,070	4.3	<250	--
Ni	<50	--	1,620	32
Zn	940	4.6	4,080	26

(a) The values given for the last six elements, Cd, Cr, Cu, Pb, Ni and Zn, are the averages of five replicates. The values given for all other elements are the averages of 15 replicates.

TABLE 21. BATTELLE AA AND ICAP DATA COMPARISON--LEACHATE[a]

Element	Ink Pigment (μg/l)		Still Bottoms (μg/l)	
	AA	ICAP	AA	ICAP
Cd	<20	<5	<20	<25
Cr	830	710	<100	<50
Cu	<50	52	12,500	13,300
Pb	5290	5070	<200	<250
Ni	<100	<50	1200	1620
Zn	1110	940	4360	4080

(a) Precision was comparable for both AA and ICAP.

TABLE 22. RECOVERY OF METALS SPIKED INTO LEACHATES FROM SOLID WASTES (BATTELLE)

Element	Analytical Method	Amount Found[(a)] in Unspiked Sample, µg/l	Amount Spiked, µg/l		RSD[(b)] of Amount Found in Spiked Sample		Percent Recovery	
			High Level	Low Level	Low Level	High Level	Low Level	High Level
INK PIGMENT								
Cd	ICAP	<5	100	500	24	7.7	88	97
	AA	<20	100	500	4.4	3.8	100	94
Cr	ICAP	710	2,000	10,000	0.5	0.9	98	98
	AA	830	2,000	10,000	1.9	3.2	116	115
Cu	ICAP	52	100	500	19	3.8	84	93
	AA	<50	100	500	5.0	2.7	126	104
Pb	ICAP	5,070	10,000	25,000	1.0	0.5	98	97
	AA	5,290	10,000	25,000	1.9	1.8	100	94
Ni	ICAP	<50	200	1,000	21	4.2	90	95
	AA	<100	200	1,000	3.8	2.1	111	102
Zn	ICAP	940	2,000	10,000	2.9	1.0	103	102
	AA	1,110	2,000	10,000	3.0	3.4	98	104
STILL BOTTOMS								
Cd	ICAP	<25	500	2,000	16	5.2	75	96
	AA	<20	500	2,000	1.2	1.9	95	90
Cr	ICAP	<50	1,000	5,000	6.9	2.9	101	104
	AA	<100	1,000	5,000	3.2	3.2	110	113
Cu	ICAP	13,300	2,000	10,000	4.1	7.3	98	96
	AA	12,500	2,000	10,000	1.6	5.2	103	95
Pb	ICAP	<250	2,000	10,000	6.9	1.9	101	103
	AA	<200	2,000	10,000	4.2	1.1	91	103
Ni	ICAP	1,620	2,000	10,000	30	10	81	99
	AA	1,200	2,000	10,000	5.2	3.3	98	98
Zn	ICAP	4,080	5,000	20,000	4.5	1.8	110	111
	AA	4,360	5,000	20,000	4.9	3.1	104	103

(a) Average of five replicates.

(b) Percent relative standard deviation from five replicates.

TABLE 23. INTERLABORATORY COMPARATIVE DATA FROM AAS ANALYSIS OF METALS IN INK PIGMENT AND STILL BOTTOMS

Compound(a)	Total Content, μg/g(b)			Leachate Content, μg/1(b)			Leaching Efficiency, Percent (c)
	Battelle Cols Labs	Southern Res Inst	Avg	Battelle Cols Labs	Southern Res Inst	Avg	
INK PIGMENTS							
Chromium	55	55	55	830	340	590	21
Copper	7	10	9	<50	<50	<50	--
Lead	250	240	245	5,290	7,540	6,420	54
Zinc	24	26	25	1,110	1,560	1,340	107
STILL BOTTOMS							
Chromium	55	39	47	<100	23	--	--
Copper	640	880	760	12,500	23,600	18,000	47
Lead	21	22	22	<200	270	--	--
Nickel	130	91	110	1,200	1,450	1,320	24
Zinc	160	220	190	4,360	5,790	5,080	53

(a) Only metals detected by both research institutes are reported here for comparison purposes.

(b) The values given are the averages of five replicate runs.

(b) The leaching efficiency represents the percent of the total content that was leached out by the solid waste leaching procedure. A single batch leaching with 1000 ml of 0.1 N NaOAc buffer, pH 4.0, per 50 gram of waste was used. The leaching efficiency was calculated as follows:

$$\%\ \text{Leaching efficiency} = \frac{\text{Avg. Leachate Content } (\mu g/1)}{50 \text{ (g of waste/1)}} \times \frac{100}{\text{Avg. Total Content } (\mu g/g \text{ of waste})}$$

TABLE 24. VOLATILE ORGANIC CONTENT OF LEACHATES FROM SOLID WASTES (BATTELLE)

Compound	Amount Spiked, μg/l	Amount Found in Unspiked Sample$^{(a)}$ μg/l	Amount Found in Unspiked Sample$^{(a)}$ RSD$^{(b)}$	Amount Found in Spiked Sample μg/l	Amount Found in Spiked Sample RSD$^{(b)}$	Percent Recovery
STILL BOTTOMS						
trans-1,2-Dichloroethene	250,000	19,000	55	210,000	11	76
1,1-Dichloroethane	50,000	158,000	21	144,000	14	(c)
Chloroform	50,000	15,000	20	56,000	10	82
1,2-Dichloroethane	250,000	99,000	16	270,000	4	68
1,1,1-Trichloroethane	50,000	15,000	15	65,000	8	100
Benzene	250,000	54	24	240,000	8	96
Carbon tetrachloride	250,000	1,600	16	240,000	10	95
Trichloroethene	250,000	190,000	11	420,000	7	92
1,1,2-Trichloroethane	50,000	360,000	11	320,000	7	(c)
Toluene	250,000	94	15	260,000	8	104
Tetrachloroethene	250,000	150,000	13	390,000	7	96
Ethylbenzene	250,000	<30	--	270,000	7	108
INK PIGMENT						
trans-1,2-Dichloroethene	2,500	<100	--	1,000	23	40
1,2-Dichloroethane	2,500	<100	--	1,300	10	52
1,1,1-Trichloroethane	500	<400	--	470	50	94
Benzene	2,500	490	30	2,700	3	76
Carbon tetrachloride	2,500	<500	--	1,700	15	68
Trichloroethene	2,500	740	28	3,000	4	90
1,1,1-Trichloroethane	500	<200	--	410	12	82
Toluene	2,500	4,300	27	5,900	3	64
Tetrachloroethene	2,500	330	20	2,900	2	104
Ethylbenzene	2,500	2,700	25	5,100	6	96

(a) Average of five replicates.

(b) Percent relative standard deviation.

(c) Could not be determined because spike level was much lower than the background level.

TABLE 25. INTERLABORATORY COMPARATIVE DATA FROM ANALYSIS OF VOLATILE ORGANICS IN INK PIGMENT AND STILL BOTTOMS

Compound	Total Content, µg/g(a)			Leachate Content, µg/l(a)			Leaching Efficiency,(b) Percent
	Battelle Cols Labs	Southern Res Inst	Avg	Battelle Cols Labs	Southern Res Inst	Avg	
INK PIGMENT							
Benzene	6	3	5	490	430	460	184
Trichloroethene	11	6	9	740	760	750	167
Toluene	68	52	64	4,300	3,200	3,750	117
Tetrachloroethene	11	4	8	330	530	430	108
Ethylbenzene	89	57	73	2,700	1,720	2,210	61
STILL BOTTOMS							
1,1-Dichloroethane	730	2,170	1,450	158,000	171,000	165,000	226
1,2-Dichloroethane	760	1,500	1,130	99,000	96,800	98,000	173
1,1,1-Trichloroethane	280	350	315	15,000	23,700	19,400	123
Trichloroethene	5,800	5,770	5,790	190,000	150,000	170,000	59
1,1,2-Trichloroethane	7,600	7,180	7,400	360,000	268,000	314,000	85
Toluene	21	29	25	94	490	290	23
Tetrachloroethene	34,000	17,200	25,700	150,000	144,000	147,000	11

(a) The values given are the averages of five replicate runs.

(b) The leaching efficiency represents the percent of the total content that was leached out by the solid waste leaching procedure. A single batch leaching with 1000 ml of 0.1 N NaOAc buffer, pH 4.0, per 50 gram of waste was used. The leaching efficiency was calculated as follows:

$$\%\ \text{Leaching efficiency} = \frac{\text{Avg. Leachate Content } (\mu g/l)}{50\ (\text{g of waste}/l)} \times \frac{100}{\text{Avg. Total Content } (\mu g/g \text{ of waste})}$$

The volatile organic content of leachates of the still bottoms and ink pigment measured by Battelle is presented in Table 24. The RSD was 15 percent or less in most cases. The percent recovery of spikes varied from 40 to 108, however, most recoveries were in the 80 to 105 percent range. The comparison of Battelle's data with SoRI's, for both total content and leachates, is shown in Table 25. These data are remarkably similar, especially since the two laboratories used different analytical methods for measurement. Battelle used a CS_2 extraction followed by GC-FID, while SoRI used Method 625 which is a purge and trap technique with detection by GC-MS.

The CS_2 extraction method used by Battelle is similar to the EPA solvent extraction method used for trihalomethanes in drinking water, except for the following three major changes: (1) an SP-2100 glass capillary column was used instead of a packed column--the improved resolution minimized the possibility of interferences and the much higher temperature permitted most of the high-boiling compounds to be eluted from the column at the end of each run; (2) a flame ionization detector was used instead of an electron capture detector--this change permitted aromatic hydrocarbons to be detected in addition to halocarbons; and (3) CS_2 was used as the solvent instead of isooctane--this selection minimized the solvent peak and permitted compounds as low-boiling as trans-1,2-dichloroethene, b.p. 48°C, to be resolved from the solvent. The main disadvantage of the CS_2 extraction method is that it does not resolve methylene chloride and lower boiling compounds from the solvent peak. A second disadvantage is that CS_2 cannot be used with a flame ionization detector when significant amounts of C_5 to C_9 saturated and olefinic hydrocarbons or other interferences are present as in a gasoline-containing sample. A saturated hydrocarbon solvent and an electron capture detector or photoionization detector would need to be used in such cases.

The CS_2 extraction method offers the following important advantages over the purge and trap GC-MS method:

(1) Requires less operator time--one person can easily extract 25 to 50 or more samples per day.

(2) Readily automated using automatic samplers in common use.

(3) Uses much less expensive instrumentation--GC instead of computerized GC-MS.

(4) Quality control is easier to maintain because of the larger number of runs that can be completed per day.

(5) Samples with extremely high levels of volatiles have much less of an adverse effect on the instrumentation.

(6) Able to determine higher-boiling components; any of the CS_2-extractable semivolatiles can be determined along with volatile constituents for samples that do not contain significant interferences.

The above advantages all contribute to the CS_2 extraction method being quicker and less costly than the purge and trap GC-MS method. The data presented in Table 25 indicate that the results obtained from the two methods in this program are comparable. Representative gas chromatograms of CS_2 extracts from leachates of ink pigment and still bottoms are shown in Figures 11 and 12, respectively. The volatile priority pollutants identified on the basis of retention times and quantified on the basis of peak areas are listed in the legends. In nearly every case the peaks are sharp and well resolved from neighboring peaks. The chromatograms also show that much higher-boiling components, in fact, any of the CS_2-extractable semivolatiles, could be determined along with the volatile components in one run if there were no significant interferences. The detection limit achieved relative to that of the semivolatiles method would be higher by a factor of 10 because the concentration factor is only 20 instead of 200. Nevertheless, the detection limit is generally about 20 to 100 μg/l which is adequate for most solid waste studies.

The semivolatile organic analyses of the leachates are more difficult to evaluate and compare due to the large number and diverse types of compounds involved. The still bottoms leachate contained few semivolatile compounds and these constituents were present at levels too low for quantitative comparison. Both laboratories identified phenol in this leachate. In contrast, the ink pigment leachate contained over a dozen semivolatile priority pollutants. A comparison of data obtained by Battelle and Southern Research Institute (SoRI) shown in Tables 26 and 27, shows good agreement in most cases. The Battelle and SoRI data for the spiked leachates are given in Tables 28 and 29. The RSD for the five replicate determinations varied from 5 to 113 with most values being around 20 to 40 percent for both laboratories. Recoveries generally were 50 to 120 percent with a few compounds having relatively poor recoveries (e.g. certain phenols). Benzidine was not recovered because only acidic conditions were used for the extractions.

Total Content

The analysis for total metals in the ink pigment and still bottom wastes is reported in Table 30. Both ICAP and AA results are included in Table 30 for silver, arsenic, antimony, cadmium, chromium, copper, lead, nickel, and zinc. These data agree well and generally the RSD is lower for ICAP. The percent recovery of spikes shown in Table 31 is good for most metals except those present in concentrations at or near the minimum detection limit.

The total volatile organic content measured by the CS_2-GC/FID method adapted for this study by Battelle is tabulated in Table 32. The RSD for replicate analyses and the percent recovery averaged 13 and 78 percent, respectively. The low recoveries are usually associated with the high background concentrations for which an inadequate amount of spikes was added, or compounds present at or near the detection limit. The comparison of Battelle and SoRI VOA data using the two different analytical methods was shown in Table 25. The excellent agreement observed suggests that either of these methods is suitable for volatile organic analysis of wastes. The advantages of the CS_2 extraction method discussed for leachates also apply to use for the total content studies. Representative gas chromatograms of CS_2

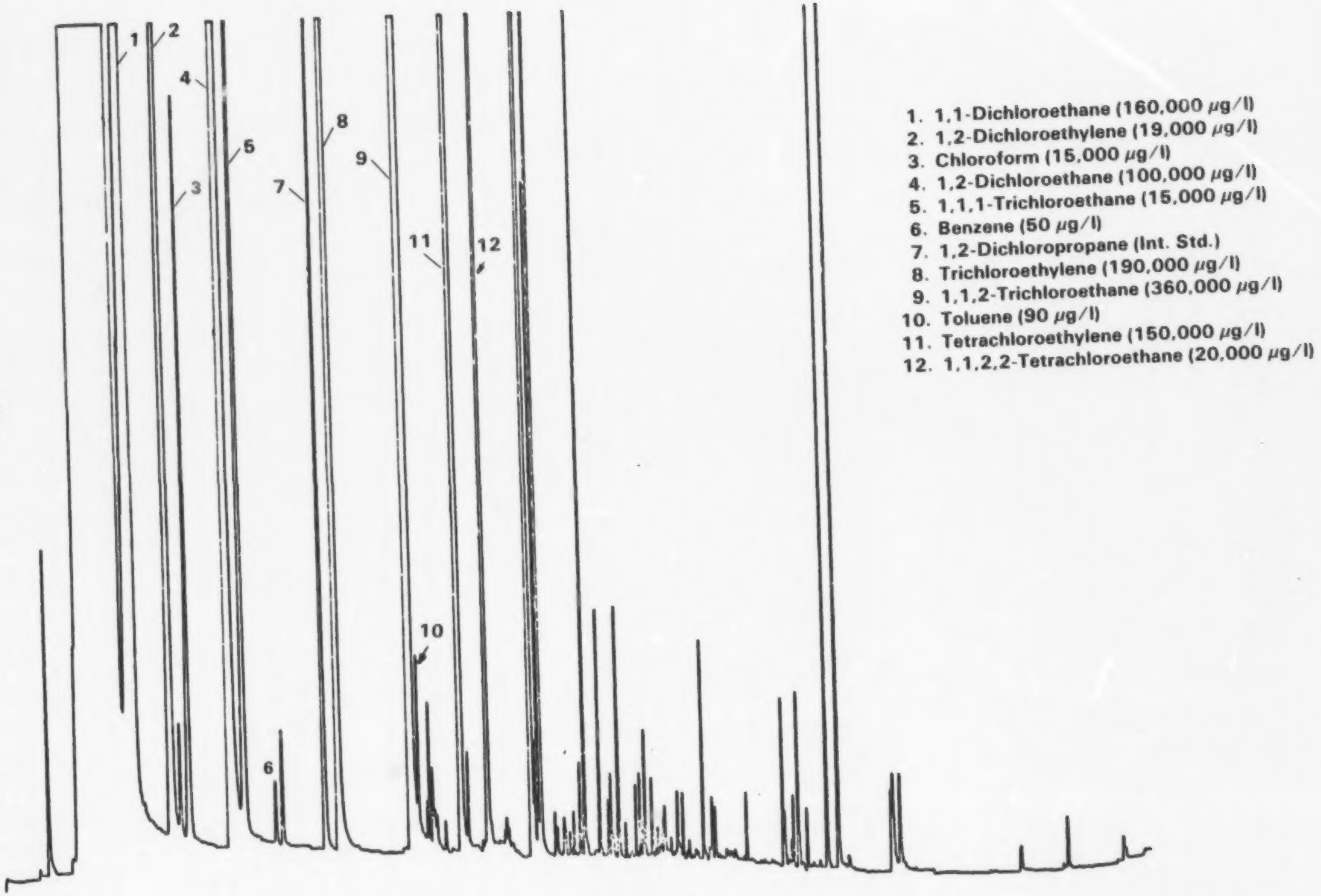


FIGURE 11. GAS CHROMATOGRAM OF CS_2 EXTRACT OF STILL BOTTOMS LEACHATE

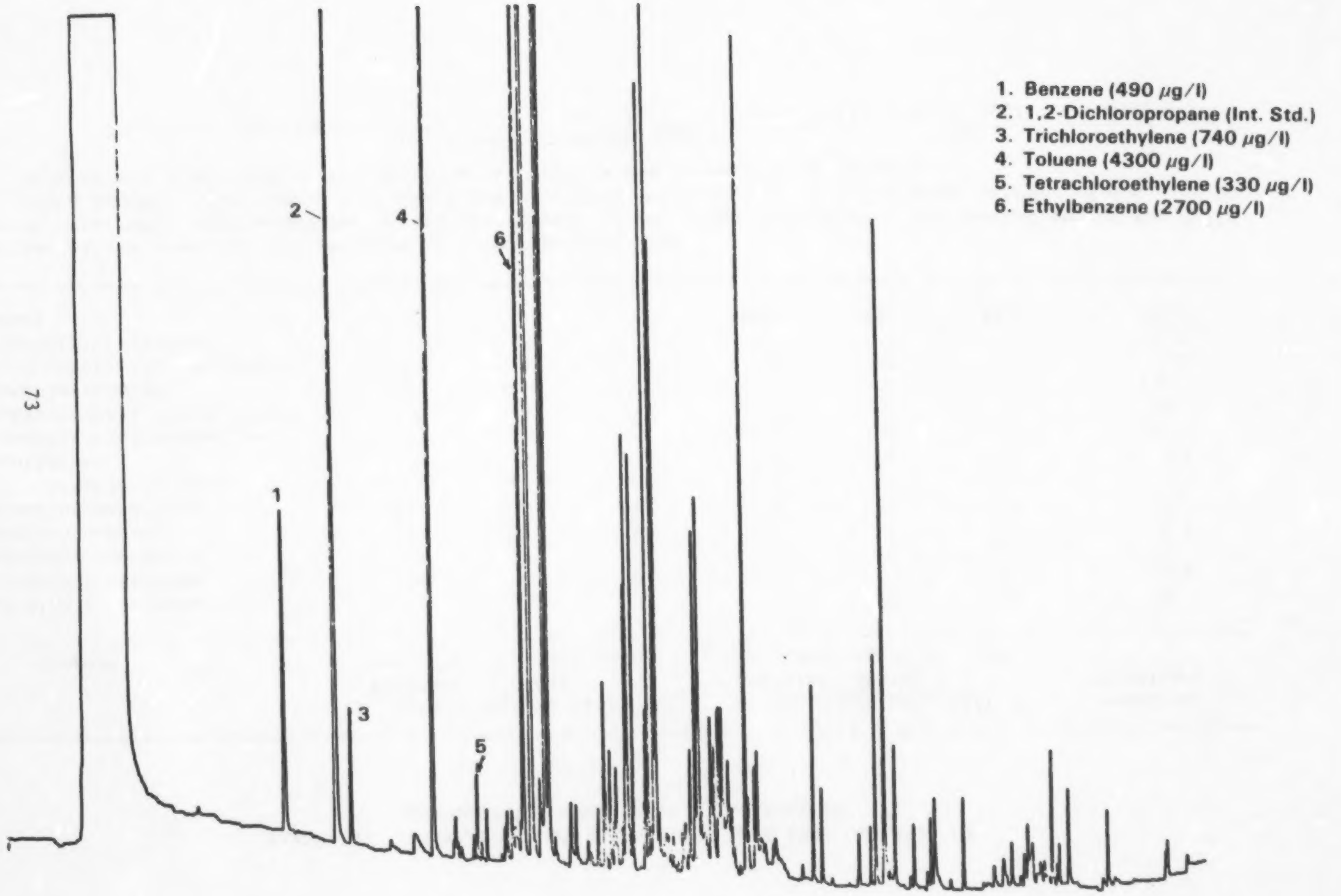


FIGURE 12. GAS CHROMATOGRAM OF CS_2 EXTRACT OF INK PIGMENT LEACHATE

TABLE 26. INTERLABORATORY COMPARATIVE DATA FROM ANALYSIS OF SEMIVOLATILE ORGANICS IN STILL BOTTOMS

Compound	Total Content, μg/g(a)			Leachate Content, μg/l(a)			Leaching Efficiency,(b) %
	Battelle Cols Labs	Southern Res Inst	Avg	Battelle Cols Labs	Southern Res Inst	Avg	
1,3-Dichlorobenzene	3	5	4	0	0	0	0
1,4-Dichlorobenzene	15	36	26	28	0	14	1.1
1,2-Dichlorobenzene	13	12	13	31	0	16	2.5
Hexachloroethane	219	181	200	25	0	13	0.1
Hexachlorobutadiene	283	328	306	0	0	0	0
1,2,4-Trichlorobenzene	29	17	23	6	0	3	0.3
Naphthalene	6	4	5	4	0	2	0.8
Hexachlorocyclopentadiene	9	2	6	0	0	0	0
4-Chlorophenyl Phenyl Ether	6	8	7	0	0	0	0
Hexachlorobenzene	175	134	155	0	0	0	0
Bis(2-ethylhexyl) Phthalate	14	3	9	14	0	7	1.6
Di-n-octyl Phthalate	3	7	5	7	0	4	1.6
Phenol	4	6	5	281	195	238	95.2

(a) The values given are the averages of five replicate runs.

(b) The leaching efficiency represents the percent of the total content that was leached out by the solid waste leaching procedure. A single batch leaching with 1000 ml of 0.1 N NaOAc buffer, pH 4.0, per 50 gram of waste was used. The leaching efficiency was calculated as follows:

$$\text{\% Leaching efficiency} = \frac{\text{Avg. Leachate Content } (\mu g/l)}{50(\text{g of waste/l})} \times \frac{100}{\text{Avg. Total Content } (\mu g/g \text{ of waste})}$$

TABLE 27. INTERLABORATORY COMPARATIVE DATA FROM ANALYSIS OF SEMIVOLATILE ORGANICS IN INK PIGMENT

Compound	Total Content, µg/g(a)			Leachate Content, µg/l(a)			Leaching Efficiency,(b) %
	Battelle Cols Labs	Southern Res Inst	Avg	Battelle Cols Labs	Southern Res Labs	Avg	
1,4-Dichlorobenzene	7	34	21	92	79	86	8.2
1,2-Dichlorobenzene	23	40	32	260	250	255	15.9
Naphthalene	26	95	61	320	560	440	14.4
Acenaphthylene	6	18	12	9	45	27	4.5
Acenaphthene	4	11	8	5	14	10	2.5
Fluorene	10	22	16	3	13	8	1.0
Phenanthrene	28	58	43	0	2	1	0.1
Fluoranthene	12	12	12	0	0	0	0
Pyrene	13	7	10	0	0	0	0
Chrysene	7	8	8	0	0	0	0
Di-n-octyl Phthalate	37	45	41	18	52	35	1.7
Benzo(b and/or k)fluoranthene	9	5	7	0	0	0	0
Benzo(a)pyrene	6	7	7	0	0	0	0
Phenol	45	68	57	2700	3100	2900	102
Pentachlorophenol	4	3	4	0	0	0	0

(a) The values given are the averages of five replicate runs.

(b) The leaching efficiency represents the percent of the total content that was leached out by the solid waste leaching procedure. A single batch leaching with 1000 ml of 0.1N NaOAc buffer, pH 4.0, per 50 gram of waste was used. The leaching efficiency was calculated as follows:

$$\%\ \text{Leaching efficiency} = \frac{\text{Avg. Leachate Content}(\mu g/l)}{50(\text{g of waste}/l)} \times \frac{100}{\text{Avg. Total Content } (\mu g/g \text{ of waste})}$$

TABLE 28. RECOVERY OF SEMIVOLATILE ORGANICS SPIKED INTO LEACHATES FROM STILL BOTTOMS

Compound	Amount Spiked, μg/l	RSD(a) of Amount Found		Percent Recovery(b)	
		BCL	SoRI	BCL	SoRI
1. 1,4-Dichlorobenzene	500	17	43	55	82
2. Bis(2-chloroethyl)ether	100	25	19	105	210
3. 1,2-Dichlorobenzene	100	15	33	57	89
4. Bis(2-chloroisopropyl)ether	500	24	9	114	108
5. N-nitrosodipropylamine	100	45	--	61	0
6. Nitrobenzene	100	15	34	58	150
7. Hexachlorobutadiene	500	17	21	70	73
8. 1,2,4-Trichlorobenzene	100	13	14	51	207
9. Isophorone	500	22	15	95	102
10. Hexachlorocyclopentadiene	100	53	36	135	71
11. Acenaphthylene	100	7	23	47	100
12. Dimethyl Phthalate	100	8	12	37	90
13. 2,6-Dinitrotoluene	100	--	33	0	74
14. 4-Chlorophenyl Phenyl Ether	100	20	14	38	188
15. Fluorene	500	8	13	45	102
16. 2,4-Dinitrotoluene	500	31	24	87	70
17. Diethyl Phthalate	500	12	22	49	222
18. Hexachlorobenzene	500	8	16	118	131
19. 4-Bromophenyl Phenyl Ether	500	12	16	41	123
20. Dibutyl Phthalate	100	16	20	45	105
21. Fluoranthene	500	13	13	38	112
22. Pyrene	100	12	17	53	100
23. Benzidine	100	--	57	0	14
24. Butyl Benzyl Phthalate	100	--	--	NA	--
25. Chrysene	500	16	19	67	160
26. 3,3'-Dichlorobenzidine	500	61	50	24	35
27. Dioctyl Phthalate	500	38	19	102	160
28. Benzo(b and/or k)fluoranthene	100	22	113	47	390
29. Tetrachlorobiphenyl	500	14	--	76	NA
30. 4,4'-DDE	500	11	--	NA	170
31. Endrin	500	33	--	170	NA
32. Hexachlorobiphenyl	100	15	--	59	NA
33. γ-BHC (Lindane)	100	24	--	80	NA
34. 4,4'-DDD	100	23	--	66	NA
35. 2-Chlorophenol	500	17	18	74	36
36. Phenol	1000	26	12	71	118
37. 2,4-Dimethylphenol	100	14	31	39	33
38. 2,4-Dichlorophenol	100	20	--	61	0
39. 2,4,6-Trichlorophenol	500	11	15	58	20
40. 2,4-Dinitrophenol	500	--	15	0	42
41. Pentachlorophenol	100	41	--	36	0
42. 4-Nitrophenol	100	--	24	0	46

(a) Percent relative standard deviation of five replicate runs.

(b) Percent recovery =

$$\frac{\text{Avg. amt. in 5 spiked runs} - \text{Avg. amt. in 5 unspiked runs}}{\text{Amount spiked}} \times 100$$

NA = Not analyzed.

TABLE 29. RECOVERY OF SEMIVOLATILE ORGANICS SPIKED INTO LEACHATES FROM INK PIGMENT

Compound	Amount Spiked, µg/l	RSD(a) of Amount Found		Percent Recovery(b)	
		BCL	SoRI	BCL	SoRI
1. 1,4-Dichlorobenzene	500	17	15	67	67
2. Bis(2-chloroethyl)ether	100	28	15	195	160
3. 1,2-Dichlorobenzene	100	24	12	80	20
4. Bis(2-chloroisopropyl)ether	500	15	12	92	77
5. N-nitrosodipropylamine	100	27	34	58	134
6. Nitrobenzene	100	24	--	95	0
7. Hexachlorobutadiene	500	24	14	88	95
8. 1,2,4-Trichlorobenzene	100	13	13	97	80
9. Isophorone	500	13	14	84	89
10. Hexachlorocyclopentadiene	100	38	7	28	91
11. Acenaphthylene	100	11	16	109	105
12. Dimethyl Phthalate	100	11	12	67	120
13. 2,6-Dinitrotoluene	100	--	--	0	83
14. 4-Chlorophenyl Phenyl Ether	100	22	24	79	80
15. Fluorene	500	17	21	85	79
16. 2,4-Dinitrotoluene	500	11	22	125	78
17. Diethyl Phthalate	500	11	--	90	0
18. N-nitrosodiphenylamine	100	--	--	NA	0
19. Hexachlorobenzene	500	28	5	147	46
20. 4-Bromophenyl Phenyl Ether	500	28	7	72	116
21. Dibutyl Phthalate	100	33	8	31	80
22. Fluoranthene	500	31	10	52	86
23. Pyrene	100	30	12	73	310
24. Benzidine	100	--	--	0	0
25. Chrysene	500	37	7	69	50
26. 3,3'-Dichlorobenzidine	500	45	10	78	18
27. Dioctyl Phthalate	500	39	27	63	94
28. Benzo(b and/or k)fluoranthene	100	35	10	57	56
29. Tetrachlorobiphenyl	500	34	--	98	NA
30. 4,4'-DDE	500	34	--	72	NA
31. Endrin	500	36	--	92	NA
32. Hexachlorobiphenyl	100	34	--	76	NA
33. γ-BHC (Lindane)	100	26	--	110	NA
34. 4,4'-DDD	100	37	--	66	NA
35. 2-Chlorophenol	500	14	29	127	26
36. Phenol	1000	15	13	89	34
37. 2,4-Dimethylphenol	100	14	21	197	78
38. 2,4-Dichlorophenol	500	16	20	153	78
39. 2,4,6-Trichlorophenol	500	11	13	138	120
40. 2,4-Dinitrophenol	500	--	11	0	98
41. Pentachlorophenol	100	16	58	97	82
42. 4-Nitrophenol	100	--	24	0	105

(a) Percent relative standard deviation of five replicate runs.

(b) Percent recovery =

$$\frac{\text{Avg. amt. in 5 spiked runs - Avg. amt. in 5 unspiked runs}}{\text{Amount spiked}} \times 100$$

NA = Not analyzed.

TABLE 30. TOTAL METALS CONTENT OF SOLID WASTES (BATTELLE)

Element	Analytical Method	Amount Found in Ink Pigment Waste[a] µg/g	RSD	Amount Found in Still Bottoms[a] µg/g	RSD
Al	ICAP	440	5.0	1,160	9.0
B	ICAP	110	2.4	13	11
Ba	ICAP	44	6.8	77	10
Be	ICAP	<0.1	--	<0.1	--
Ca	ICAP	735	11	2,910	24
Co	ICAP	<0.1	--	<0.5	--
Fe	ICAP	300	20	10,480	6.7
Mg	ICAP	4,800	3.8	1,090	6.1
Mn	ICAP	35	28	69	25
Mo	ICAP	10	3.8	<1	--
Sn	ICAP	<0.6	--	<3	--
Ti	ICAP	4.9	15	9.1	1.4
V	ICAP	3.2	62	5.3	9.1
Y	ICAP	<0.1	--	0.6	16
Se	ICAP	<3	--	<15	--
Tl	ICAP	<8	--	<40	--
Ag	ICAP	<0.2	--	<1	--
Ag	GFAAS	NA	--	1	--
As	ICAP	3.3	14	17	19
As	GFAAS	NA	--	1.6	9
Sb	ICAP	<0.2	--	<10	--
Sb	GFAAS	0.3	18	NA	--
Cd	ICAP	<0.1	--	<0.5	--
Cd	GFAAS	0.2	26	NA	--
Cr	ICAP	46	3.3	47	7.9
Cr	FAAS	55	2.9	55	7.4
Cu	ICAP	6	15	630	3.2
Cu	FAAS	6.7	9.0	636	3.6
Pb	ICAP	222	2.0	20	20
Pb	FAAS	254	--	21	20
Ni	ICAP	1	--	130	5.5
Ni	GFAAS	1.5	27	129	5.7
Zn	ICAP	19	5.8	154	8.4
Zn	FAAS	24	17	163	4.7
Hg	CVAAS	NA	--	0.7	12

(a) The values given for the last 10 elements Ag, As, Sb, Cd, Cr, Cu, Pb, Ni, Zn, and Hg, are the averages of five replicates. The values for all other elements are the averages of 15 replicates.

NA = Not analyzed.

TABLE 31. RECOVERY OF METALS SPIKED INTO SOLID WASTE (BATTELLE)

Element	Analytical Method	Amount Found[a] in unspiked Sample ug/g	Amount Spiked, ug/g		RSD[c] of Amount Found in Spiked Sample		Percent Recovery	
			Low Level	High Level	Low Level	High Level	Low Level	High Level
INK PIGMENT								
Cd	ICAP	<0.1	0.1	1	—	94	(b)	72
Cd	FAAS	<0.2	0.2	1	12	6.9	200	130
Cd	GFAAS	0.2	0.2	—	20	—	255	--
Cr	ICAP	46	50	250	0.9	2.9	98	98
Cr	FAAS	55	50	250	1.0	2.8	92	115
Cu	ICAP	6	25	100	3.7	5.3	96	98
Cu	FAAS	6.7	25	100	3.4	2.7	101	94
Pb	ICAP	222	250	1,000	1.2	2.0	94	90
Pb	FAAS	254	250	1,000	1.1	3.1	98	100
Ni	ICAP	1	1	5	11	9.0	110	90
Ni	FAAS	<1	1	5	12	3.4	100	118
Ni	GFAAS	1.5	1	5	28	4.5	250	109
Zn	ICAP	19	25	100	1.2	3.8	100	99
Zn	FAAS	24	25	100	2.2	2.1	100	102
Sb	GFAAS	0.3	1	5	16	11	54	84
STILL BOTTOMS								
Cr	ICAP	47	25	100	4.5	3.0	96	101
Cr	FAAS	55	25	100	2.0	2.6	116	112
Cu	ICAP	630	250	1,000	5.6	1.8	94	92
Cu	FAAS	636	250	1,000	3.3	1.6	99	95
Pb	ICAP	20	25	100	6.4	7.2	100	104
Pb	FAAS	21	25	100	3.8	4.2	104	98
Ni	ICAP	130	100	500	3.6	1.4	92	97
Ni	FAAS	129	100	500	1.1	2.9	96	96
Zn	ICAP	154	100	500	7.0	6.0	97	108
Zn	FAAS	163	100	500	3.4	6.4	108	107
Be	ICAP	<0.1	0.1	0.5	--	55	200	200
Ag	ICAP	<1	0.5	2	--	--	(b)	(b)
Ag	GFAAS	0.1	0.5	2	44	31	84	37
As	ICAP	15	2	10	13	5.2	--	60
As	GFAAS	1.6	2	10	6.2	5.8	64	62
Hg	CVAAS	0.7	2	10	5.4	7.2	96	73

(a) Average of five replicates.

(b) Not detected.

(c) Percent relative standard deviation from five replicates.

TABLE 32. TOTAL VOLATILE ORGANIC CONTENT OF SOLID WASTES (BATTELLE)

Compound	Amount Spiked, µg/g	Amount Found in Unspiked Sample$^{(a)}$ µg/g	RSD	Amount Found in Spiked Sample µg/g	RSD	Percent Recovery
STILL BOTTOMS						
trans-1,2-Dichloroethene	5,000	<10	—	3,700	16	74
1,1-Dichloroethane	1,000	730	16	1,500	10	77
Chloroform	1,000	<5	—	890	19	89
1,2-Dichloroethane	5,000	760	12	5,100	7	87
1,1,1-Trichloroethane	1,000	280	23	1,200	9	92
Benzene	5,000	25	10	4,300	9	86
Carbon tetrachloride	5,000	<10	—	4,700	9	94
Trichloroethene	5,000	5,800	11	10,000	16	84
1,1,2-Trichloroethane	1,000	7,600	11	8,100	21	50
Toluene	5,000	21	8	5,000	15	100
Tetrachloroethene	5,000	34,000	14	36,000	22	40
Ethylbenzene	5,000	<1	—	5,500	19	110
INK PIGMENT						
trans-1,2-Dichloroethene	50	<10	--	25	32	50
1,1-Dichloroethane	10	<10	--	2.2	16	22
Chloroform	10	<5	--	5.2	13	52
1,2-Dichloroethane	50	<10	--	33	18	66
1,1,1-Trichloroethane	10	<10	--	5.3	(c)	53
Benzene	50	6	17	47	11	83
Carbon tetrachloride	50	<10	--	36	19	72
Trichloroethene	50	11	13	55	12	88
1,1,2-Trichloroethane	10	5	12	4.3	29	0
Toluene	50	68	15	120	17	104
Tetrachloroethene	50	11	11	55	12	88
Ethylbenzene	50	89	10	140	16	102

(a) Average of five replicates.

(b) Percent relative standard deviation.

(c) RSD not calculated because only two values were available.

extracts of ink pigment and still bottoms are shown in Figures 13 and 14, respectively. Although very complex patterns of large amounts of extractable components were obtained, especially in the case of still bottoms, the volatile priority pollutants of interest appear in the early portion of the chromatograms where adequate resolution of individual components is generally achieved. The chromatograms also show that despite the large amounts of extractable components, most are eluted from the column during the temperature programming to 250°C that was used. The temperature could be raised to 300°C for more complete elution of high-boiling components without adversely affecting the column. This type of thermal cleaning of the GC column cannot be achieved when the conventional packed column for volatile organics, one percent SP-1000 on Carbopak C, is used because of the greater retentiveness and much lower temperature limitation of the SP-1000 column.

The unspiked sample data for semivolatile organics was shown in Tables 26 and 27. In general, the agreement between the BCL and SoRI data is very good, with the average values seldom differing by more than a factor of two. Spiked samples data are given in Tables 33 and 34. Recoveries were generally 50 to 150 percent, with reasonably good agreement between SoRI and BCL. However, some of the spike levels (e.g. dibenzo(a,h)-anthracene) were too low to detect.

Comparison of Leaching Efficiency

The analysis of the leachate to determine potentially mobile or leachable compounds, and the analysis of the solid waste, for total content of those compounds, enables a calculation of leaching efficiency to be made. The leaching efficiencies are included in Table 23 for metals, Table 25 for organics, and Tables 26 and 27 for semivolatile organics. In general, both metals and organics were leached to a greater extent from the ink pigment sample than from the still bottom sample. This result is probably due to the fact that the ink pigment waste is more readily dispersed in water than the still bottom sample and contains less insoluble material that might retain components by adsorption.

For semivolatile organics the leaching efficiency was quite low (generally less than 10 percent) except for phenol, a highly water-soluble compound for which the leaching was essentially complete. Leaching efficiency for metals ranged from 20 to 100 percent.

The leaching efficiency data for volatile organics (Tables 26 and 27) are interesting in that 200 percent recoveries are noted for the more volatile compounds, and a rapid decrease in apparent leaching efficiency is observed with increasing boiling point. We believe that the anomalously high leaching efficiency values for the more volatile compounds is primarily due to loss of volatiles during sample handling. Since a much smaller quantity of waste (five grams) is weighed out and extracted for the total content determination than for the leaching procedure, the relative loss of volatiles will be greater in the total content method, thus resulting in a lower apparent total content and a calculated high leaching efficiency.

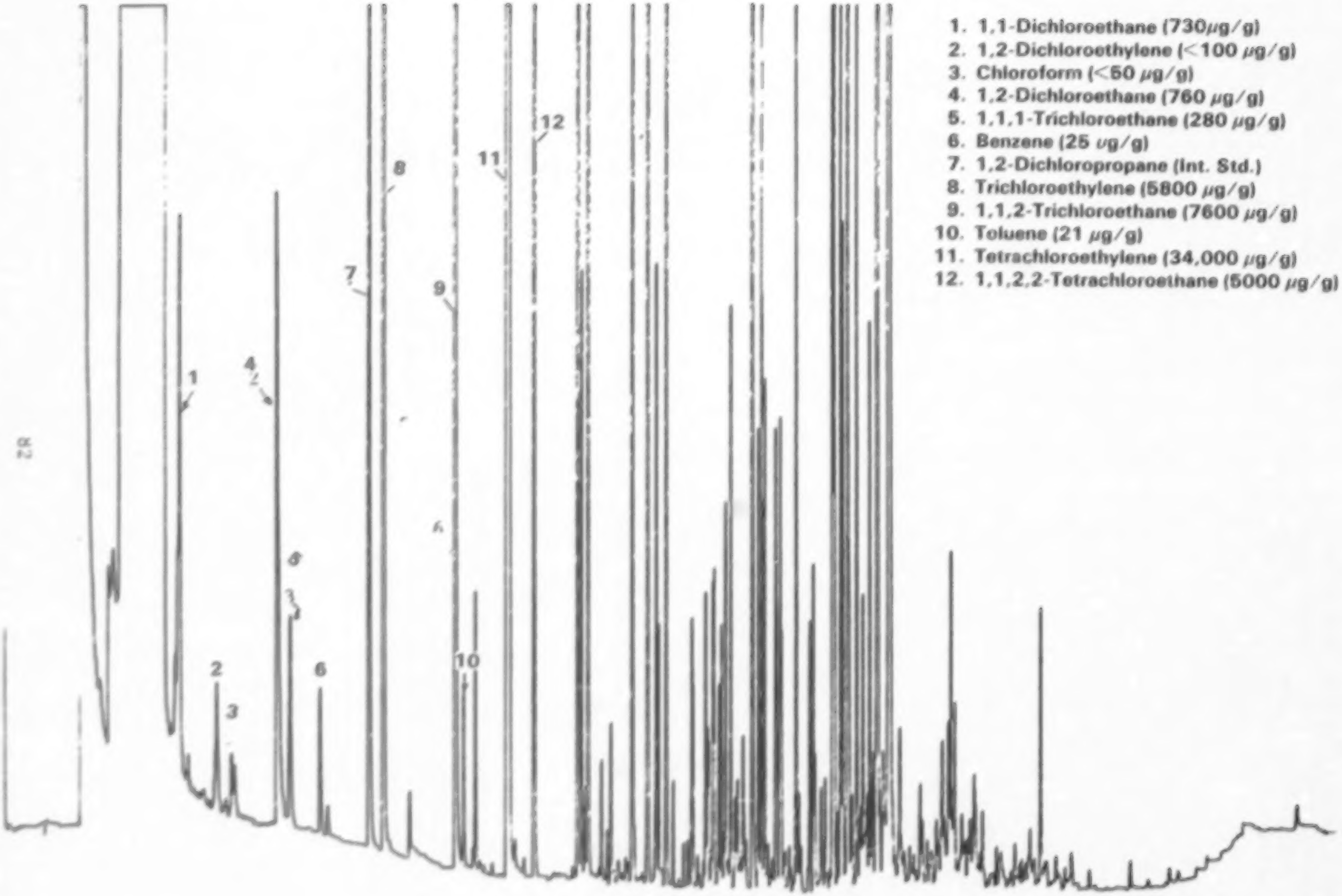


FIGURE 13. GAS CHROMATOGRAM OF CS_2 EXTRACT OF STILL BOTTOMS FOR TOTAL CONTENT ANALYSIS

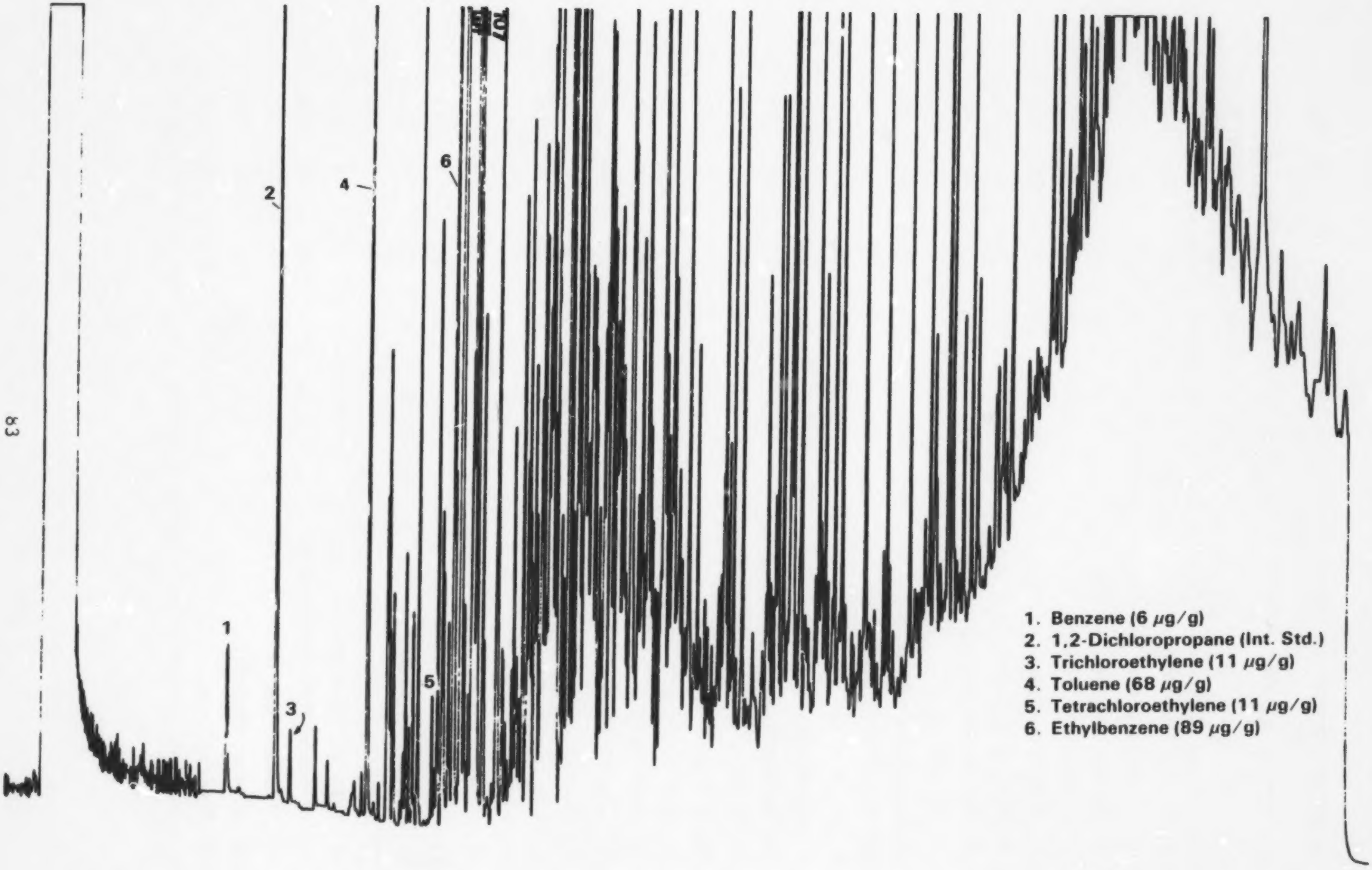


FIGURE 14. GAS CHROMATOGRAM OF CS_2 EXTRACT OF INK PIGMENT FROM TOTAL CONTENT ANALYSIS

TABLE 33. RECOVERY OF SEMIVOLATILE ORGANICS SPIKED INTO STILL BOTTOMS BASED ON TOTAL CONTENT ANALYSIS

Compound	Amount Spiked, µg/g	RSD(a) of Amount Found BCL	RSD(a) of Amount Found SoRI	Percent Recovery(b,c) BCL	Percent Recovery(b,c) SoRI
1. 1,3-Dichlorobenzene	29.2	12	40	83	160
2. 1,4-Dichlorobenzene	214	6	44	29	65
3. Bis(2-chloroethyl)ether	10.0	28	21	120	88
4. 1,2-Dichlorobenzene	63.6	11	17	88	51
5. Hexachloroethane	1020	10	38	106	86
6. Bis(2-chloroisopropyl)ether	10.0	14	17	70	79
7. N-nitrosodipropylamine	10.0	--	36	0	46
8. Nitrobenzene	10.1	--	79	0	151
9. Hexachlorobutadiene	1800	6	40	19	86
10. 1,2,4-Trichlorobenzene	140	9	37	49	79
11. Isophorone	10.1	16	54	109	63
12. Bis(2-chloroethoxy)methane	10.1	19	16	89	208
13. Naphthalene	27.0	7	30	67	68
14. Hexachlorocyclopentadiene	10.1	20	38	59	38
15. 2-Chloronaphthalene	9.6	--	14	0	62
16. Acenaphthylene	10.1	18	30	109	67
17. Acenaphthene	2520	7	31	14	40
18. Dimethyl Phthalate	10.1	24	17	64	100
19. 2,6-Dinitrotoluene	10.1	--	21	0	78
20. 4-Chlorophenyl Phenyl Ether	79.2	16	42	126	66
21. Fluorene	10.0	19	17	80	94
22. 2,4-Dinitrotoluene	10.2	--	33	0	87
23. Diethyl Phthalate	11.1	24	30	117	95
24. Diphenylhydrazine	10.0	--	22	0	134
25. N-Nitrosodiphenylamine	10.0	--	50	0	150
26. Hexachlorobenzene	8.1	--	24	0	240
27. 4-Bromophenyl Phenyl Ether	10.3	22	21	97	105
28. Phenanthrene	10.1	19	6	79	42
29. Dibutyl Phthalate	10.1	32	14	99	92
30. Fluoranthene	10.0	28	22	60	102

TABLE 33 (Continued)

Compound	Amount Spiked, µg/g	RSD(a) of Amount Found		Percent Recovery(b,c)	
		BCL	SoRI	BCL	SoRI
31. Pyrene	10.1	20	31	109	105
32. Benzidine	10.1	--	50	0	53
33. Butyl Benzyl Phthalate	10.1	--	14	0	92
34. Bis(2-ethylhexyl) Phthalate	33.1	32	44	280	110
35. Chrysene/Benzo(a)anthracene	10.1	25	16	98	120
36. 3,3'-Dichlorobenzidine	10.1	45	89	6	18
37. Dioctyl Phthalate	10.1	38	21	13	0
38. Benzo(b and/or k)fluoranthene	22.1	29	15	72	52
39. Benzo(a)pyrene	10.4	36	14	77	109
40. Indeno(1,2,3,-c,d)Pyrene	0.05	--	--	0	0
41. Dibenzo(a,h)anthracene	0.10	--	--	0	0
42. Benzo(g,h,i)perylene	10.1	48	20	20	98
43. 2-Chlorophenol	10.0	60	64	10	56
44. 2-Nitrophenol	10.1	--	00	0	0
45. Phenol	42.9	5	57	77	68
46. 2,4-Dimethylphenol	10.0	10	101	53	31
47. 2,4-Dichlorophenol	10.1	7	40	129	64
48. 2,4,6-Trichlorophenol	10.1	5	45	129	73
49. 4-Chloro-3-methylphenol	10.0	--	51	0	68
50. 2,4-Dinitrophenol	10.0	--	--	0	0
51. 2-Methyl-4,6-dinitrophenol	10.0	--	--	0	0
52. Pentachlorophenol	10.0	16	28	70	49
53. 4-Nitrophenol	10.0	--	--	0	0

(a) Percent relative standard deviation of five replicate runs.

(b) Percent recovery =

$$\frac{\text{Avg. amt. in 5 spiked runs} - \text{Avg. amt. in 5 unspiked runs}}{\text{Amount spiked}} \times 100$$

(c) The total content method described by Southern Research Institute (SoRI) was used by Battelle's Columbus Laboratories (BCL) and SoRI.

TABLE 34. RECOVERY OF SEMIVOLATILE ORGANICS SPIKED INTO INK PIGMENT BASED ON TOTAL CONTENT ANALYSIS

Compound	Amount Spiked, µg/g	RSD(a) of Amount Found		Percent Recovery(b,c)	
		BCL	SoRI	BCL	SoRI
1. 1,3-Dichlorobenzene	8.5	28	29	29	120
2. 1,4-Dichlorobenzene	54.9	29	21	20	52
3. Bis(2-chloroethyl)ether	10.0	41	23	50	73
4. 1,2-Dichlorobenzene	85.2	23	14	23	224
5. Hexachloroethane	10.0	51	30	40	218
6. Bis(2-chloroisopropyl)ether	10.0	37	41	20	82
7. N-nitrosodipropylamine	10.0	--	43	0	24
8. Nitrobenzene	50.2	--	22	10	35
9. Hexachlorobutadiene	10.2	69	19	39	117
10. 1,2,4-Trichlorobenzene	11	24	21	27	205
11. Isophorone	10.1	44	14	30	210
12. Bis(2-chloroethoxy)methane	40.3	36	17	35	72
13. Naphthalene	161	16	9	6	54
14. Hexachlorocyclopentadiene	10.1	--	49	0	12
15. 2-Chloronaphthalene	9.6	--	21	0	74
16. Acenaphthylene	111	24	13	41	79
17. Acenaphthene	85.6	24	12	35	236
18. Dimethyl Phthalate	35.2	32	14	37	76
19. 2,6-Dinitrotoluene	10.1	--	18	0	436
20. 4-Chlorophenyl Phenyl Ether	10.0	31	45	40	89
21. Fluorene	60.2	37	13	43	82
22. 2,4-Dinitrotoluene	61.0	40	16	25	86
23. Diethyl Phthalate	11.1	36	23	27	64
24. Diphenylhydrazine	10.0	--	19	0	175
25. N-Nitrosodiphenylamine	10.0	--	28	0	113
26. Hexachlorobenzene	8.1	31	14	50	75
27. 4-Bromophenyl Phenyl Ether	10.3	30	47	29	70
28. Phenanthrene	86.2	19	12	33	11
29. Dibutyl Phthalate	10.1	32	16	69	64
30. Fluoranthene	11.2	25	73	30	85

TABLE 34 (Continued)

Compound	Amount Spiked, µg/g	RSD(a) of Amount Found		Percent Recovery(b,c)	
		BCL	SoRI	BCL	SoRI
31. Pyrene	116	34	7	43	64
32. Benzidine	10.0	--	28	0	9
33. Butyl Benzyl Phthalate	10.1	--	27	0	71
34. Bis(2-ethylhexyl) Phthalate	161	28	34	120	26
35. Chrysene/Benzo(a)anthracene	60.9	36	19	99	90
36. 3,3'Dichlorobenzidine	10.1	95	66	55	82
37. Dioctyl Phthalate	10.1	40	34	180	109
38. Benzo(b and/or k)fluoranthene	132	36	13	74	49
39. Benzo(a)pyrene	61.9	34	26	90	114
40. Indeno(1,2,3,-c,d)Pyrene	0.5	--	--	0	0
41. Dibenzo(a,h)anthracene	0.1	--	--	0	0
42. Benzo(g,h,i)perylene	60.1	32	25	22	137
43. 2-Chlorophenol	30.4	24	12	33	150
44. 2-Nitrophenol	10.1	--	14	0	117
45. Phenol	13.1	15	13	115	92
46. 2,4-Dimethylphenol	31.3	15	23	35	51
47. 2,4-Dichlorophenol	10.1	22	25	50	131
48. 2,4,6-Trichlorophenol	10.1	30	30	30	125
49. 4-Chloro-3-methylphenol	10.0	--	24	0	134
50. 2,4-Dinitrophenol	10.0	--	23	0	140
51. 2-Methyl-4,6-dinitrophenol	10.0	--	15	0	110
52. Pentachlorophenol	86	25	21	49	73
53. 4-Nitrophenol	79	--	47	0	112

(a) Percent relative standard deviation of five replicate runs.

(b) Percent recovery =

$$\frac{\text{Avg. amt. in 5 spiked runs} - \text{Avg. amt. in 5 unspiked runs}}{\text{Amount spiked}} \times 100$$

(c) The total content method described by Southern Research Institute (SoRI) was used by Battelle's Columbus Laboratories (BCL) and SoRI.

STATISTICAL TREATMENT OF THE DATA

A large amount of important data was collected from the laboratory experiments which were conducted during this program. These data were used in an empirical manner to gain insight into the performance characteristics of the methods studied.

Descriptive statistics, including mean recoveries, standard deviations and relative standard deviations, were calculated. These statistics were used to make qualitative comparisons among the various leaching methods.

Formal application of statistical tests or estimation procedures to establish "significant" differences in performance characteristics (such as precision) among the leaching methods is inappropriate for this program. First, such an application requires the establishment of a well-defined set of parameters, relating to the characteristic of interest. Secondly, if statistical testing is required, the formal hypotheses involving the parameters of interest which are to be tested must be established. If the comparisons are to be based on interval estimation techniques, then the comparisons of interest must be specified in terms of the proper combination of the population parameters. No set of parameters was defined nor any formal statistical hypotheses proposed, therefore, the retrospective calculation of test statistics or confidence intervals is not meaningful.

This discussion does not imply that the data are not meaningful, however, these data cannot be used in a formal inferential manner. The descriptive statistics, such as mean recoveries and standard deviations based on replicate analyses, were invaluable for empirically assessing differences in method characteristics.

SECTION VII

QUALITY ASSURANCE

The results of quality assurance efforts are demonstrated partly by the documentation that included sample logging and sample traceability, and recording of experimental work and experimental data. Quality assurance was also demonstrated by results of replicate analyses of blanks, standards and spiked samples. These results are given in the many tables shown throughout this report.

The quality control efforts included a study of the performance of the analytical methods. These studies were carried out early in the program in order not only to assess the performance but to provide information on control limits and to provide a basis of comparison of performance of the leaching process.

Four analysis methods were studied including inductively coupled argon plasma (ICAP) and atomic absorption spectrophotometry (AAS) for metals determination, gas chromatography-mass spectrometry (GC-MS) for volatile organic (purgeable) compounds, and GC-MS for semivolatile organic compound determinations.

The general scheme for these studies included replicate analyses of blanks and spiked samples from which precision was calculated. In the case of analysis for metals and volatile organic compounds, this early work also included assessment of accuracy through spike and recovery studies.

The samples (blanks and spikes) were carried through the analysis procedure in order to estimate performance of the analysis procedure rather than simply instrumental performance. In general, the performance indicated by these experiments was as expected based on performance measured on other programs using the same or similar analysis methods. The relative standard deviations of results of analyses of solutions done within 1 day are expected to be of the order of a few percent. On the other hand, the same type measurements done over a period of days and weeks will show greater deviation. This effect is more pronounced with regard to determinations of organic compounds than for determinations of metals because the control of the methodologies for determinations of metals is technically more advanced.

VOLATILE ORGANICS

The precision data obtained for GC-MS analysis of volatile organics in distilled water using EPA Method 624 are given in Table 35. The response

TABLE 35. PRECISION DATA FOR GC-MS ANALYSIS OF VOLATILE ORGANICS IN WATER USING EPA METHOD 624

Compound	Internal Standard Used (a)	Relative Response Factor(b) Obtained at Given Level (c)			RSD(d) of Relative Response Factor(b) Obtained at Given Level (c)		
		5 μg/l	20 μg/l	100 μg/l	5 μg/l	20 μg/l	100 μg/l
Dichloromethane	A	2.05	2.43	2.94	7.8	3.0	2.2
Trichlorofluoromethane	A	1.79	2.52	2.34	1.9	3.2	2.6
Acrylonitrile	A	ND	0.34	0.43	-	7.2	4.5
1,1-Dichloroethene	A	1.11	1.44	1.62	2.9	1.2	2.2
1,1-Dichloroethane	A	2.43	3.28	3.80	1.3	2.1	1.6
(E)-1,2-Dichloroethene	A	1.20	1.57	1.33	1.3	0.9	1.9
Trichloromethane	A	3.90	4.59	4.28	3.7	2.1	1.2
1,2-Dichloroethane	A	0.10	0.16	0.23	11.9	5.0	5.7
1,1,1-Trichloroethane	B	0.66	0.66	0.52	6.3	2.9	1.7
Tetrachloromethane	B	0.29	0.49	0.59	3.5	1.4	2.2
Bromodichloromethane	B	0.01	0.04	0.06	0	4.0	2.7
1,2-Dichloropropane	B	ND	0.01	0.03	-	10.2	3.9
(E)-1,3-Dichloro-1-propene	B	0.39	0.55	0.65	3.9	3.1	1.4
Trichloroethene	B	0.38	0.48	0.52	4.1	4.1	2.4
Benzene	B	1.31	1.39	1.48	7.4	3.7	0.6
Dibromochloromethane	B	0.31	0.45	0.53	1.9	3.1	1.5
1,1,2-Trichloroethane	B	0.39	0.42	0.45	3.0	2.6	1.3
(Z)-1,3-Dichloro-1-propene	C	0.28	0.40	0.54	2.0	2.2	20.1
Tribromomethane	C	0.26	0.42	0.55	4.5	4.3	0.4
1,1,2,2-Tetrachloroethane	C	0.19	0.30	0.35	3.0	1.3	2.2
Tetrachloroethene	C	0.32	0.44	0.49	4.7	2.3	1.9
Toluene	C	0.84	0.95	0.98	4.5	1.9	1.9
Chlorobenzene	C	1.00	1.19	1.30	1.7	4.2	1.4
Ethylbenzene	C	0.41	0.54	0.57	3.7	1.3	0.2

(a) A = Bromochloromethane; B = 2-Bromo-1-chloropropane; C = 1,4-Dichlorobutane. All internal standards were present at 50 μg/l.

(b) Relative response factor = $\frac{\text{Amount of int. std}}{\text{Area of int. std}} \times \frac{\text{Area of compound}}{\text{Amount of compound}}$.

(c) Each value is an average obtained from three runs.

(d) RSD = percent relative standard deviation.

ND = Not detected.

factors for the three different levels agree quite well in most cases and the relative standard deviations are generally less than 10 percent. Direct injections of standard solutions in methanol were also run to determine if the purge and trap part of the analysis scheme introduced significant variations. The results, given in Table 36, indicate similar performance except for acrylonitrile which is not purged from water completely. Recovery data and precision data obtained from the analysis of a simulated leachate, POTW sludge supernatant, spiked with volatile organics are given in Table 37. The recoveries were generally greater than 75 percent and the precision was similar to that observed for spiked distilled water.

SEMIVOLATILE ORGANICS

GC-MS precision data from the analysis of calibration/spike standard solutions of semivolatile organics were generated in two different ways:

- An initial precision study in which the standards were analyzed repetitively
- Precision of the standard solutions interspersed with the authentic leachate samples (one standard solution every fourth sample).

Precision data were generated using a capillary column as well as a packed column. The precision data resulting from the initial precision study are shown in Table 38. The base/neutral compounds were analyzed on a packed column containing 3 percent SP-2250 on 80/100-mesh Supelcoport, and the phenols were analyzed on a packed column containing 1 percent SP-1240-DA on 80/100-mesh Supelcoport. As can be seen from the percent relative standard deviations, the response factors are precise and change minimally with changes in concentration. Packed column precision data generated from analysis of equivalent standard solutions interspersed among the samples over a period of 4 weeks are presented in Table 39. Under these conditions the response factors are not as precise. This result is not unexpected because analysis of actual samples may cause changes in the character of the column. Also over a period of several weeks, the mass spectrometric performance may vary somewhat, causing variations in the response factor. Somewhat unexpectedly, the response factors at the two lower levels (50 and 200 µg/l) were generally more equivalent and larger than the response factors at the high level (500 ug/l). The medium level (200 ug/l) generally showed the lowest percent relative standard deviation. More confidence can be placed on the RSD for the 200 ug/l standard because, as a result of the protocol, two of these standards were analyzed for each of the 50 ug/l standard and the 500 ug/l standard. One possible reason for the lower response factors for the 500 ug/l levels is saturation of the electron multiplier.

Precision data for the analysis of standard solutions interspersed with samples and analyzed on the SE-52 capillary column for Task 6 are shown in Table 40. A modified list of compounds was used for the Task 6 studies. The overall precision is not as good as for the packed column and the detection of the phenols was not as good. However, the precision of the analyses at the highest level was very good.

TABLE 36. PRECISION DATA FOR GC-MS ANALYSIS OF VOLATILE ORGANICS BY DIRECT INJECTION OF STANDARDS

Compound	Internal Standard Used(a)	Relative Response Factor(b) Obtained at Given Level(c,e)			RSD(d) of Relative Response Factor(b) Obtained at Given Level(c,e)		
		5 µg/l	20 µg/l	100 µg/l	5 µg/l	20 µg/l	100 µg/l
Dichloromethane	A	3.87	3.95	3.92	2.0	1.3	7.4
Trichlorofluoromethane	A	1.33	1.65	1.62	2.2	1.7	1.8
Acrylonitrile	A	1.30	1.49	1.32	0.0	1.9	1.9
1,1-Dichloroethene	A	1.42	1.52	1.42	8.2	1.9	2.0
1,1-Dichloroethane	A	3.30	3.55	3.46	1.7	0.0	8.3
(E)-1,2-Dichloroethene	A	0.97	1.10	1.08	3.0	0.0	2.7
Trichloromethane	A	4.46	4.20	3.96	1.7	0.0	7.3
1,2-Dichloroethane	A	0.09	0.01	0.19	3.3	1.6	1.5
1,1,1-Trichloroethane	B	0.54	0.60	0.51	5.6	0.0	7.1
Tetrachloromethane	B	0.50	0.65	0.59	0.0	0.0	4.9
Bromodichloromethane	B	0.02	0.05	0.06	17.5	0.0	0.0
1,2-Dichloropropane	B	<0.01	0.02	0.23	36	0.0	12.3
(E)-1,3-Dichloro-1-propene	B	0.67	0.49	0.60	24	4.2	0.0
Trichloroethene	B	0.42	0.50	0.46	1.2	0.0	3.9
Benzene	B	1.04	1.41	1.36	4.2	1.8	2.2
Dibromochloromethane	B	0.46	0.55	0.35	0.0	0.0	0.0
1,1,2-Trichloroethane	B	0.47	0.50	0.46	1.6	0.6	0.6
(Z)-1,3-Dichloro-1-propene	C	1.15	0.55	0.45	13	0.0	0.6
Tribromomethane	C	0.43	0.55	0.55	1.3	0.0	0.0
1,1,2,2-Tetrachloroethane	C	0.26	0.33	0.30	0.0	0.9	0.82
Tetrachloroethene	C	0.36	0.44	0.38	0.0	0.7	0.7
Toluene	C	0.74	0.80	0.74	3.9	0.0	3.9
Chlorobenzene	C	1.07	1.15	1.07	2.7	0.0	2.7
Ethylbenzene	C	0.43	0.48	0.46	2.0	1.2	1.1

(a) A = Bromochloromethane; B = 2-Bromo-1-chloropropane; C = 1,4-Dichlorobutane. All internal standards were present at 50 µg/l.

(b) Relative response factor = $\frac{\text{Amount of int. std.}}{\text{Area of int. std.}} \times \frac{\text{Area of compound}}{\text{Amount of compound}}$

(c) Each value is an average obtained from three runs.

(d) RSD = percent relative standard deviation.

(e) The amount of standard analyzed was converted to the corresponding level of µg/l in water that would apply when EPA Method 624 is used.

TABLE 37. PRECISION DATA FOR GC-MS ANALYSIS OF VOLATILE ORGANICS IN A POTW SLUDGE SUPERNATANT USING EPA METHOD 624

Compound	Internal Standard Used(a)	Amount Found, µg/l in Given Sample(b)		RSD(d) of Amount Found in Given Sample		Percent Recovery(e) of Spike
		Unspiked	Spiked(c)	Unspiked	Spiked	
Dichloromethane	A	16	143	8	0	254
Trichlorofluoromethane	A	0	9	—	11	18
Acrylonitrile	A	0	25.8	—	6	52
1,1-Dichloroethene	A	0	36.7	—	11	73
1,1-Dichloroethane	A	1.2	46.0	15	8	90
(E)-1,2-Dichloroethene	A	0.8	11.9	16	9	22
Trichloromethane	A	7.1	54.3	4	7	94
1,2-Dichloroethane	A	5.0	37.6	16	4	65
1,1,1-Trichloroethane	B	123	133	5	10	20
Tetrachloromethane	B	—	37.6	—	10	75
Bromodichloromethane	B	—	40.0	—	9	80
1,2-Dichloropropane	B	—	42.5	—	3	85
(E)-1,3-Dichloro-1-propene	B	—	42.0	—	9	84
Trichloroethene	B	3.3	48.0	2	9	90
Benzene	B	1.5	64.1	4	9	125
Dibromochloromethane	B	0.1	50.2	0	7	100
1,1,2-Trichloroethane	B	—	50.6	—	8	101
(Z)-1,3-Dichloro-1-propene	C	—	41.5	—	9	83
Tribromomethane	C	—	51.2	—	9	102
1,1,2,2-Tetrachloroethane	C	24.4	70.7	<1	9	93
Tetrachloroethene	C	29.1	72.5	<1	10	87
Toluene	C	142	181	1	8	78
Chlorobenzene	C	60.9	114	1	5	106
Ethylbenzene	C	27.8(b)	70.9	<1(b)	6	106

(a) A = Bromochloromethane; B = 2-Bromo-1-chloropropane; C = 1,4-Dichlorobutane
All internal standards were present at 50 µg/l.

(b) The values given are the averages of five replicates. Response factors obtained previously from standards in distilled water at 100 µg/l were used for all calculations.

(c) Spiked at 50 µg/l.

(d) RSD = percent relative standard deviation

(e) Percent recovery = $\frac{\text{Amount in spiked sample} - \text{Amount in unspiked sample}}{50} \times 100.$

TABLE 38. PRECISION DATA FOR GC-MS ANALYSIS OF SEMIVOLATILE ORGANICS IN STANDARD SOLUTIONS

[illegible]

TABLE 39. PRECISION DATA FOR GC-MS ANALYSIS OF SEMIVOLATILE ORGANICS USING A PACKED COLUMN OVER A PERIOD OF 4 WEEKS (μg/l)

Compound	Relative Response Factor Obtained at the Given Level(a,b,c)			Percent Relative Standard Deviation Obtained at the Given Level		
	50(d)	200(e)	500(d)	50	200	500
1,4-Dichlorobenzene	0.519	0.494	0.354	17	20	17
Bis(2-chloroethyl)ether	0.242	0.255	0.192	29	25	37
Hexachloroethane	0.209	0.211	0.154	15	16	33
N-Nitrosodipropylamine	ND	0.065	0.033	-	32	10
Nitrobenzene	0.228	0.259	0.190	36	24	35
1,2,4-Trichlorobenzene	0.533	0.520	0.354	12	15	17
Isophorone	ND	0.304	0.153	-	26	54
Bis(2-chloroethoxy)methane	0.311	0.366	0.259	37	20	29
Naphthalene	1.05	1.05	0.691	14	18	20
2-Chloronapthalene	0.898	0.920	0.616	12	16	19
Acenaphthylene	1.23	1.26	0.838	15	16	16
Acenaphthene	0.811	0.801	0.528	11	14	18
Dimethyl Phthalate	1.112	1.01	0.682	11	14	14
2,6-Dinitrotoluene	0.183	0.229	0.159	24	18	16
4-Chlorophenyl Phenyl Ether	0.529	0.530	0.348	12	14	16
Diethyl Phthalate	0.919	0.929	0.596	20	16	16
N-Nitrosodiphenylamine (as Diphenylamine)	0.603	0.638	0.420	13	13	15
Phenanthrene (&/or Anthracene-DO)	1.71	1.41	0.932	13	7	13
Pyrene	1.69	1.53	0.997	8	9	14
Benzidine	ND	0.042	0.014	-	25	41
Butyl Benzyl Phthalate	0.625	0.619	0.393	19	14	20
Chrysene	1.25	1.08	0.667	22	23	29
3,3'-Dichlorobenzidine	0.369	0.313	0.176	37	34	41
Dioctyl Phthalate	1.12	1.05	0.728	13	25	16
Benzo(b and/or k)fluoranthene	1.21	1.04	0.624	22	26	32
A-BHC (Hexachlorocyclohexane)	0.195	0.198	0.133	9	11	20
Heptachlor	0.128	0.158	0.115	23	22	34
Aldrin	0.169	0.166	0.114	43	29	37
Heptachlor Epoxide	0.141	0.128	0.093	16	18	27
Tetrachlorobiphenyl	0.509	0.461	0.300	8	9	11
4,4'-DDE	0.447	0.389	0.260	6	8	21
Endrin	0.028	0.033	0.019	60	32	60
Endosulfan Sulfate	0.109	0.103	0.066	23	35	68
2-Chlorophenol	0.295	0.316	0.330	9	10	10
2-Nitrophenol	0.182	0.208	0.225	7	9	9
Phenol	0.200	0.207	0.211	12	5	7
2,4-Dimethylphenol	0.173	0.195	0.211	6	9	14
2,4-Dichlorophenol	0.372	0.399	0.398	9	9	10
2,4,6-Trichlorophenol	0.294	0.313	0.309	8	9	12
4-Chloro-3-methyphenol	0.221	0.249	0.266	8	5	10
2,4-Dinitrophenol	ND	0.027	0.075	-	93	15
4,6-Dinitro-o-cresol	0.045	0.070	0.151	64	28	9
Pentachlorophenol	0.263	0.254	0.254	29	15	15
4-Nitrophenol	ND	0.031	0.035	-	32	14

(a) D_{10}-anthracene was used as the internal standard at a level that corresponds to 250 μg/l in water prior to extraction.

(b) Relative response factor = (Amt of Int Std/Area of Int Std) x (Area of Compound/Amt of Compound).

(c) The amounts injected on column were 20, 80, and 200 ng which correspond to the given levels of 50, 200, and 500 μg/l in water prior to extraction.

(d) Average of 5 to 6 values.

(e) Average of 10 to 15 values.

ND = Not detected.

TABLE 40. PRECISION DATA FOR GC-MS ANALYSIS OF SEMIVOLATILE ORGANICS USING A CAPILLARY COLUMN OVER A PERIOD OF 2 WEEKS (μg/l)

Compound	Relative Response Factor Obtained at the Given Level[a,b,c]			% Relative Standard Deviation Obtained at the Given Level		
	50	200	500	50	200	500
Bis(2-chloroethyl)ether	0.462	0.578	0.513	11	36	3
1,4-Dichlorobenzene	0.868	0.825	0.629	2	23	8
1,2-Dichlorobenzene	0.496	0.467	0.391	3	23	4
Bis(2-chloroisopropyl)ether	0.686	0.822	0.623	5	45	3
Hexachloroethane	0.114	0.095	0.123	6	33	4
N-nitrosodipropylamine	0.018	0.021	0.040	20	33	6
Nitrobenzene	0.083	0.107	0.058	11	38	14
Isophorone	0.360	0.564	0.629	14	42	6
Bis(2-chloroethoxy)methane	0.389	0.471	0.497	16	33	3
1,2,4-Trichlorobenzene	0.517	0.500	0.422	2	13	2
Naphthalene	1.659	1.709	1.002	5	21	13
Hexachlorobutadiene	0.260	0.251	0.211	4	6	4
Hexachlorocyclopentadiene	0.005	0.011	0.028	41	27	13
Acenaphthylene	0.999	1.081	0.939	6	11	7
Dimethyl Phthalate	0.326	0.468	0.549	21	20	3
Acenaphthene	0.827	0.930	0.794	5	10	10
2,4-Dinitrotoluene	0.008	0.013		36	38	
Fluorene	0.878	0.977	0.792	4	7	6
4-Chlorophenyl Phenyl Ether	0.240	0.273	0.307	5	3	1
Diethyl Phthalate	0.218	0.352	0.478	17	21	7
4-Bromophenyl Phenyl Ether	0.129	0.148	0.189	1	11	1
Hexachlorobenzene	0.124	0.135	0.118	5	15	2
G-BHC (Lindane)	0.036	0.041		7	14	
Phenanthrene	0.989	1.123	0.958	3	2	6
Dibutyl Phthalate	0.188	0.298	0.484	10	18	8
4,4'-DDE	0.097	0.126	0.162	2	11	3
Dieldrin	0.064	0.089	0.115	16	26	8
Endrin	0.002	0.006	0.007	29	39	8
4,4'-DDD	0.058	0.079	0.132	3	17	2
3,3'-Dichlorobenzidine	0.048	0.067	0.139	1	21	3
Bis(2-ethylhexyl) Phthalate	0.062	0.080	0.124	8	12	4
Dioctyl Phthalate	0.065	0.094	0.147	18	15	1
Fluoranthene	0.930	1.212	1.019	4	5	2
Chrysene	0.399	0.501	0.381	1	11	4
Benzo(k)fluoranthene	0.315	0.382	0.297	6	11	4
Benzo(a)pyrene	0.340	0.423	0.299	6	13	3
Indeno(1,2,3-c,d)pyrene	0.170	0.238	0.154	4	13	2
Dibenzo(a,h)anthracene	0.211	0.330	0.186	7	16	1
Benzo(g,h,i)perylene	0.348	0.485	0.308	5	18	2
Phenol	0.160	0.527	0.288	4	53	1
2-Chlorophenol	0.063	0.290	0.303	24	51	7
2,4-Dimethylphenol	0.188	0.316	0.360	10	36	3
2,4-Dichlorophenol	ND	0.147	0.126	-	66	17
2,4,6-Trichlorophenol	ND	0.082	0.062	-	72	26
Pentachlorophenol	ND	0.034	ND	-	75	-

(a) D_{10}-anthracene was used as the internal standard at the 100 ng level.

(b) Relative response factor = (Amt of Internal Standard/Area of Internal Standard) x (area of Compound/Amount of Compound).

(c) The amounts injected were 20, 80, and 200 ng which correspond to the given levels of 50, 200, and 500 μg/l in water prior to extraction.

(d) Average of 5 to 6 values.

(e) Average of 10 to 15 values. ND = Not detected.

In calculating concentrations of compounds in waste samples and leachates, average response factors were used; thus, the RSD of the response factors obtained over several weeks gives an indication of variability in compounds in a leachate that is attributable to variation in response factor.

In all these studies, the internal standard performance was used to judge the validity of a particular analysis run. If the response (peak area count) of the internal standard was different by more than a factor of two from expected, the data for that run were ignored and the sample was reanalyzed.

METALS

The percent relative standard deviation (RSD) and percent recovery of metals that were determined by inductively coupled argon plasma are shown in Tables 41 and 42. The RSDs for the medium and high concentration are of the order of 2 percent or less for most metals. Metals for which the RSD is greater than 2 percent include boron, molybdenum, tin and antimony. The behavior of these metals is erratic either because of blank problems (boron in particular), because of their refractory nature (boron, molybdenum, and tin), or because of typically poor performance (tin). Tin in acid solution tends to precipitate as metastannic acid at the higher concentrations and may have precipitated molybdenum by occlusion. The RSDs shown for the low concentration range typically from about 1 to 15 percent, which is expected because the concentrations are near the detection limits and thus more subject to influence of variability of background than at higher concentrations. The RSDs above 15 percent are the result of background (blank) concentrations that are greater than the spike concentration. Thus, the analytical signal from the spiked concentration is overwhelmed by the blank concentration in these cases.

The percent recovery data for the ICAP method show the recoveries of spikes are generally in the range of 90 to 110 percent. The recoveries of a few elements are outside this range for the same reasons that cause the comparatively poor precision for the same elements.

The results for precision and recovery studies on the atomic absorption spectrophotometric (AAS) method are shown in Tables 43 and 44. The precisions and recoveries at all concentrations are within the normal limits. The relative standard deviations are somewhat higher than those shown for the ICAP method. This result also is expected because the nebulizing system and the excitation source for the ICAP are more stable and thus more repeatable than the similar systems for the AAS.

The RSDs obtained for Tasks 5 and 6 (analyses of replicated leachings) indicate expected larger RSDs as compared to the analysis method precision. The variability of leaching is included in the calculated results from Tasks 5 and 6. The differences in RSDs appear to be a function of leaching method rather than a function of concentration as is the case with the analysis method studies. For example, for leachates from the baghouse dust sample, Table 10, manganese was found at nearly the same concentration in all

TABLE 41. PRECISION DATA FOR ICAP ANALYSIS OF METALS IN DISTILLED WATER

Element	Amount Found in Blank(a), μg/ℓ	Amount Added as Spike at Given Level(b), μg/ℓ			Amount Found as Spike at Given Level(a,b), μg/ℓ			Percent Recovery of Spike at Given Level(a,b)			Percent Relative Standard Deviation at Given Level(b)		
		Low	Med	High	Low	Med	High	Low	Med	High	Low	Med	High
Al	271	500	2500	10000	626	2730	10130	70.9	98.4	98.6	13.1	0.9	1.1
B	692	50	250	1000	58	800	1260	-1270	43.5	57.3	38	19.1	19.7
Ba	6.0	25	125	500	30	132	518	94.7	100.5	102.4	4.0	0.6	0.7
Be	1.3	5	25	100	5.7	27.5	110	87.6	104.8	109.1	3.3	0.5	0.6
Cd	0.9	25	125	500	28.4	131	513	109.9	103.9	102.4	12.7	0.8	0.9
Co	1.4	50	250	1000	55.8	257	1010	108.8	102.1	101.1	6.1	0.9	1.1
Cr	5.8	50	250	1000	52.9	263	1040	94.2	103.0	103.5	7.7	1.4	0.3
Cu	43	50	250	1000	67	258	998	48.7	86.2	95.5	15.0	2.5	1.5
Fe	105	50	250	1000	133	334	1080	56.8	91.7	97.5	9.8	6.3	1.0
Pb	20	500	2500	10000	526	2530	9970	101.2	100.5	99.5	0.5	0.8	0.7
Mn	3.1	25	125	500	30.1	134	519	107.8	104.9	103.2	11.0	1.9	0.9
Mo	6.4	100	500	2000	106	243	473	99.2	47.4	23.3	1.0	4.1	9.3
Ni	45	150	750	3000	193	793	3060	98.4	99.7	100.6	3.9	0.4	0.8
Sn	-7.9(c)	250	1250	5000	228	359	467	94.5	29.4	9.5	2.6	4.8	12.8
Ti	30	100	500	2000	139	457	1520	109.4	85.5	74.6	3.8	0.9	1.6
V	4.1	100	500	2000	104	492	1870	100.2	97.6	93.5	0.9	0.7	1.4
Y	2.5	50	250	1000	52.1	257	1020	99.2	101.9	101.9	0.8	0.5	0.5
Zn	75	25	125	500	71.6	151	555	-12	60.9	96.1	22.8	3.4	4.0
Ag	8.3	-	250	1000	--	247	946	--	95.5	93.6	--	1.7	0.5
As	32	-	1250	5000	--	1244	4950	--	96.9	98.4	--	3.5	0.5
Sb	15	-	1250	5000	--	134	228	--	9.5	4.2	--	20.1	20.2
Se	11	-	1250	5000	--	1230	5060	--	97.5	101.0	--	1.4	0.7
Tl	-59(c)	-	1250	5000	--	962	5060	--	81.7	102.5	--	3.8	1.0

(a) Each value is the average obtained from five separate digests.
(b) Low = 10x detection limit; Med = 50x detection limit; High = 200x detection limit.
(c) Negative values indicate contamination in blanks.

TABLE 42. PRECISION DATA FOR ICAP ANALYSIS OF METALS IN A DISTILLED WATER LEACHATE FROM A POTW SLUDGE

Element	Amount Found in Unspiked Leachate(a), µg/ℓ	Amount Added as Spike at Given Level(b), µg/ℓ			Amount Found as Spike at Given Level(a,b), µg/ℓ			Percent Recovery of Spike at Given Level(a,b)			Percent Relative Standard Deviation at Given Level(b)		
		Low	Med	High	Low	Med	High	Low	Med	High	Low	Med	High
Al	1390	500	2500	10000	1890	3840	11300	98.9	97.8	99.2	3.4	1.7	0.8
B	1510	50	250	1000	336	1030	1090	-2350	-193	-42	6.8	34	7.5
Ba	528	25	125	500	553	658	1060	99.3	103.9	105.8	0.7	2.1	1.7
Be	0.4	5	25	100	5.9	28.5	111	110.4	112.3	111	1.7	2.5	0.9
Cd	51	25	125	500	71	174	554	81.3	98.1	100.5	1.4	1.4	1.0
Co	15	50	250	1000	65	268	1030	100.1	101.2	101.4	2.0	1.2	1.0
Cr	163	50	250	1000	206	409	1170	87.7	98.7	100.4	1.6	1.8	1.0
Cu	160	50	250	1000	101	318	1050	-118	62.9	88.9	2.2	2.4	1.7
Fe	5300	50	250	1000	5340	5530	6310	82.0	92.1	100.7	0.7	2.5	2.1
Pb	259	500	2500	10000	746	2730	10100	97.3	99.0	98.2	1.0	1.1	1.0
Mn	972	25	125	500	998	1100	1513	105.8	105.7	108.2	0.8	2.2	1.7
Mo	9	100	500	2000	110	503	1880	100.8	98.8	93.3	1.3	1.0	0.6
Ni	250	150	750	3000	392	982	3220	94.8	97.6	98.9	1.7	1.2	1.0
Sn	25	250	1250	5000	229	508	2320	81.8	38.7	46.0	5.7	22.4	12.0
Ti	36	100	500	2000	135	384	1220	99.0	69.4	59.1	2.2	7.4	3.6
V	9	100	500	2000	113	521	2030	103.7	102.4	100.9	0.9	0.8	0.8
Y	8	50	250	1000	60	266	1030	103.6	102.9	101.9	0.7	0.7	0.9
Zn	3450	25	125	500	3390	3520	4000	-228	60.2	110.9	0.9	2.4	2.4
Ag	15	-	250	1000	--	91	106	--	30.6	9.1	-	17.0	16.0
As	76	-	1250	5000	--	1470	5160	--	111.3	101.7	-	3.3	0.6
Sb	40	-	1250	5000	--	557	2120	--	41.4	41.6	-	11.7	7.7
Se	23	-	1250	5000	--	1390	5400	--	109.1	107.6	-	2.6	0.5
Tl	-7(c)	-	1250	5000	--	1060	4970	--	85.7	99.6	-	5.3	0.9

(a) Each value is the average obtained from five separate digests.

(b) Low = 10x detection limit; Med = 50x detection limit; High = 200x detection limit.

(c) Negative value indicates contamination in blank.

TABLE 43. PRECISION DATA FOR AAS ANALYSIS OF METALS IN DISTILLED WATER

Element	Amount Found in Unspiked Leachate[a], μg/ℓ	Amount Added as Spike at Given Level[b], μg/ℓ			Amount Found as Spike at Given Level[a,b], μg/ℓ			Percent Recovery of Spike at Given Level[a,b]			Percent Relative Standard Deviation at Given Level[b]		
		Low	Med	High	Low	Med	High	Low	Med	High	Low	Med	High
Be	<20	5	25	100	<20	29	110	--	114	114	--	4.5	4.8
Cd	57	25	125	500	93	180	580	140	95	104	18	6.5	4.4
Cr	170	50	250	1000	240	440	1300	136	109	117	8.1	19.0	4.1
Cu	158	50	250	1000	130	370	1100	(b)	84	90	7.1	4.9	5.2
Ni	248	150	750	3000	360	720	3200	72	63	97	7.3	6.5	3.6
Zn	3340	25	125	500	3300	3500	4000	(b)	128	140	2.6	3.5	6.0
Hg	<0.3	1.6	10	25	1.1	8.6	21	71	86	83	10.2	4.1	5.6

(a) Number of replicates = 5.
(b) Spike level too low to be meaningful.

TABLE 44. PRECISION DATA FOR AAS ANALYSIS OF METALS IN A DISTILLED WATER LEACHATE FROM A POTW SLUDGE

Element	Amount Added as Spike at Given Level(b), μg/ℓ			Amount Found as Spike at Given Level(a,b), μg/ℓ			Percent Recovery of Spike at Given Level(a,b)			Percent Relative Standard Deviation at Given Level(b)		
	Low	Med	High	Low	Med	High	Low	Med	High	Low	Med	High
Be	5	25	100	<20	28	99	--	113	99	--	3.0	1.1
Cd	25	125	500	34	134	534	134	107	107	13	4.1	1.0
Cr	50	250	1000	<100	258	970	--	103	97	--	4.2	3.4
Cu	50	250	1000	<100	298	990	--	119	99	--	2.8	1.1
Ni	150	750	3000	140	360	3120	93	48	104	21	13.0	4.2
Zn	25	125	500	<20	182	520	--	146	104	--	6.0	8.2
Hg	1.6	10	25	1.4	8.5	22	85	85	88	4.2	4.1	0

(a) Number of replications = 5.

leachates (except one) but the RSDs for manganese varied from 86 percent for the extraction procedure (EP) to less than 10 percent for sodium citrate leachates using the NBS leaching device.

Recovery studies using spiked leachates show results (Table 22) similar to those shown for the analysis method--usually between 90 and 110 percent recovery. This result indicates that the elements extracted are determined without apparent interelement interference even though the concentrations of a few elements were relatively high. Thus, matrix interferences, if present, were adequately controlled by the analysis system.

Improvement in assessing data quality would include replicate analyses of replicate leachings. This addition would add extra degrees of freedom and would provide for opportunity for more formal statistical evaluation of data.

Also, more could have been done in evaluating the variables in the leaching procedure. For example, while many experiments would have been involved, a study could have been made of effect of leach time, of leach temperature, of solid to liquid ratio, of the number of leachings, and of the value of adding internal standards to the waste before leaching. These experiments would indicate which steps in the procedure are critical and what degree of control is essential for each step.

SECTION VIII

DISCUSSION

SELECTION OF WASTES

The Resource Conservation and Recovery Act covers an extremely broad range of solid waste types in respect to composition and physical properties. The amounts of water, solids, acids, bases, metals, total organics, extractable organics, volatile organics, or immiscible oils that a waste contains may range from less than one percent to nearly 100 percent. These compositional differences can profoundly affect the physical properties of the waste such as viscosity, dispersibility, wettability, filterability, and water miscibility. Consequently the composition of a waste can profoundly affect waste behavior in any batch leaching procedure that might be proposed for assessing the potential mobility of components in the waste. Since an objective of this program was the development of a solid waste leaching procedure that would be applicable to as many different types of wastes as possible, it was particularly important that types of wastes that might be expected to cause problems in a leaching procedure be included in the study. It was reasoned that if it could be demonstrated that a leaching procedure could handle the more difficult types of wastes, it could be reasonably expected that the procedure could handle most or all of the simple wastes which are easier to handle.

A total of 23 different wastes became available for this program (see Table 3). Nearly half of the wastes obtained(11) either contained at least 97 percent water or were completely miscible with water and therefore were considered entirely unsuitable for the development of a solid waste leaching procedure. Two of the wastes were oily wastes containing more than 20 percent oil. Since the oil would be almost completely mobile it was decided that a total content analysis would sufficiently characterize the potential mobility of such wastes. Consequently those two wastes were considered inappropriate for the program. Three of the wastes, namely electroplating sludge, fly ash, and baghouse dust, were expected to contain only trace amounts of organic components. Since mobility of organic components was of major importance in the program only one of these inorganic wastes, baghouse dust, was selected for study. The pulp and paper sludge had a relatively high solids content, 20 percent, but was excluded from the study because it was expected to contain primarily cellulosic fiber and very few solvent extractable organic priority pollutants.

The seven remaining wastes including baghouse dust were selected for at least part of the study on the basis of relatively high solids content (>15 percent) and with the exception of baghouse dust, the likelihood of containing significant amounts of extractable organic compounds.

Dewatered POTW sludge from Cincinnati was selected for the Task 3 and Task 4 studies because it represented a composite from many industries and was expected to contain detectable amounts of a variety of organic and inorganic priority pollutants. It was also available earlier in the program than most of the other wastes that subsequently became of interest. The organic still bottoms sample was of particular interest because it had a high solids content and was expected to have a high extractable organic content. This waste also represented a rather acidic waste. The coal gasification tar waste was of interest because this viscous tar was expected to be a very difficult material to work with in an aqueous leaching system. The ink pigment waste was of interest because it was highly alkaline and unlike the other wastes had a gelatinous consistency. The other two wastes selected, a pharmaceutical waste and a latex paint sludge, had solids contents of about 15 percent and were expected to be high in extractable organic constituents. Initial leaching studies showed that very few organic priority pollutants were leached from these two samples. Consequently these wastes were given less attention than the other selected wastes.

As described above, the wastes selected for the program covered a range of pHs and physical consistencies. These wastes were high in solids content and contained significant amounts of several organic and inorganic priority pollutants. However, the available wastes did not include those representative of the more difficult to handle, more toxic, or more heterogeneous solid wastes that are being generated by various industries. It would have been helpful to have had additional such wastes available to challenge the leaching procedure more severely.

SELECTION OF LEACHING MEDIA

The seventeen leaching media studied are described in Table 6. The acetic acid titration, EP procedure, was used as a reference medium. The pH and buffering capacity that it provides is intended to simulate those parameters of municipal landfill leachates. Distilled water was used as a second reference medium. Distilled water simulates rainwater and contains no analytical interferences or components, such as acetate, that would be toxic in a bioassay. The acetate and citrate buffered systems were designed to provide a pH and acid capacity similar to that of the EP procedure when the maximum amount of acetic acid is required. Citrate was used in place of acetate to provide complexing ability, antioxidant or reducing activity, a less solvent-extractable acid, and possibly a less toxic medium. The effect of changing pH, buffer capacity, and influence of ammonium ion was studied using a variety of citrate media. Butyrate was used as a medium to determine the effect of a more lipophilic component that is frequently present in municipal landfill leachates. Ferrous sulfate and sodium hydrosulfite were studied to determine the effect of reducing media. A detergent was studied to simulate the effect of surface-active components such as soaps that might be present in some landfill leachates. A nonionic detergent was used to avoid any pH effects or inactivation by ionic species. The University of

Wisconsin synthetic leachate was included as a medium that best simulates a municipal landfill leachate despite the analytical interferences introduced.

It was concluded from the study that of the various media described above, distilled water is the leaching medium of choice. It is nontoxic, does not introduce any analytical interferences, is easy to use, and leaches organic components as well as any of the other media studied. The various media containing citrate or acetate often leach much higher levels of metals than are leached by distilled water but the increases vary over a wide range depending upon the particular metal involved and the nature of the waste. Ammonium citrate gave results similar to those of sodium citrate. The ammonium ion would cause less analytical interference but would be considerably more toxic in many bioassays. The addition of reducing agents or a detergent had little significant effect. The addition of ferrous sulfate interfered very significantly with the metal analyses. The University of Wisconsin synthetic leachate contains this interference as well as pyrogallol which interferes with the organic analysis and bioassays. The use of butyrate had little effect on the leaching of metals. It also seriously interfered with the organic analyses.

LEACHATE ANALYSIS METHODS

Metal Analyses

Methods used for sample preparation of leachates prior to analysis for metals were taken from "Methods for Chemical Analysis of Waters and Wastes."(42) Either Method 4.1.3 (HNO_3 digestion) or the HNO_3 - H_2O_2 procedure for graphite furnace analysis was used, as described previously.

Method 4.1.3 appeared to work well for most metals, as indicated by the quantitative spike recoveries obtained. However less than quantitative recoveries were found for some elements, including molybdenum and tin. Low recoveries for these elements occurred in the precision study with either distilled water or POTW leachate as the matrix. The reason for low recoveries for these elements is not fully understood, although one possible explanation is given under "Metals" in the Quality Assurance Section of this report. Low recovery was also found for boron. It is likely that boron was lost during the digestion step as the sample was taken to near dryness.

It is recommended in "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants" that antimony be analyzed on the sample prepared by Method 4.1.3. However, very low spike recoveries (<10 percent) were commonly found in samples prepared using this method. Conversely, spiked samples prepared using the HNO_3 - H_2O_2 digestion recommended for flameless analysis demonstrated quantitative recoveries. For this reason, antimony was analyzed in samples prepared by the HNO_3 - H_2O_2 digestion method. Recovery of As, Sb, Se, and Tl were normally quantitative using the HNO_3 - H_2O_2 preparation also. Silver recovery was frequently low, although the presence of chlorine in the samples is highly likely, resulting in the precipitation of AgCl.

Method 4.1.3 involves two steps that require interpretation by the analyst. First, it is necessary to stop the digestion prior to complete dryness of the sample. The final concentration found could be affected by the point of termination, either due to incomplete digestion if halted too soon or due to volatilization of some elements if allowed to become too dry. Second, the reflux process is repeated an unspecified number of times, until the "digestion is complete". The actual concentration found may be a function of the number of reflux cycles used.

Volatile Organic Compounds

The CS_2 extraction method used by Battelle was similar to the EPA solvent extraction method used for trihalomethanes in drinking water, except for the following three major changes: (1) an SP-2100 glass capillary column was used instead of a packed column--the improved resolution minimized the possibility of interferences and the much higher temperature permitted most of the high-boiling compounds to be eluted from the column at the end of each run; (2) a flame ionization detector was used instead of an electron capture detector--this change permitted aromatic hydrocarbons to be detected in addition to halocarbons; and (3) CS_2 was used as the solvent instead of isooctane--this selection minimized the solvent peak and permitted compounds as low-boiling as trans-1,2-dichloroethene, b.p. 48°C, to be resolved from the solvent. The main disadvantage of the CS_2 extraction method is that it does not resolve methylene chloride and lower boiling compounds from the solvent peak. A second disadvantage is that CS_2 cannot be used with a flame ionization detector when significant amounts of C_5 to C_9 saturated and olefinic hydrocarbons or other interferences are present as in a gasoline-containing sample. A saturated hydrocarbon solvent and an electron capture detector or photoionization detector would need to be used in such cases.

The CS_2 extraction method offers the following important advantages over the purge and trap GC-MS method:

(1) It requires less operator time--one person can easily extract 25 to 50 or more samples per day.

(2) It can be readily automated using automatic samplers in common use.

(3) It uses much less expensive instrumentation--GC instead of computerized GC-MS.

(4) Quality control is easier to maintain because of the larger number of runs that can be completed per day.

(5) Samples with extremely high levels of volatiles have much less of an adverse effect on the instrumentation.

(6) Much higher-boiling components, in fact, any of the CS_2-extractable semivolatiles, can be determined along with the volatile components in samples that do not contain significant interferences.

The results obtained on this program using the CS_2 extraction method were comparable to those obtained using the purge and trap method. The chromatographic peaks obtained for volatile components were all sharp and well resolved from neighboring peaks.

The detection limit of the method is higher than the purge-and-trap method by a factor of about 100 and higher than the semivolatiles method by a factor of 10. Nevertheless, the detection limit is generally about 20 to 100 μg/l which is adequate for most solid waste studies.

Semivolatile Organic Compounds

The method used for the solvent extraction of leachates and determination of semivolatile organic priority pollutants was a simplified version of EPA Method 625. The modifications were designed to decrease the number of steps involved and decrease the amount of technician time required without affecting precision or accuracy. The modifications were as follows:

(1) A 300-ml sample was used instead of 1000 ml.

(2) A single extraction with 50 ml of methylene chloride per 100 ml of water was used instead of three extractions each with 6 ml of methylene chloride per 100 ml of water.

(3) The extraction was performed only under acidic conditions instead of under basic conditions followed by acidic conditions.

(4) A single extract containing both the neutrals and acids was analyzed using as SE-52 glass capillary column instead of analyzing two separate fractions, base/neutrals and acids, using a 3 percent SP-2250 packed column and a 1 percent SP-1240-DA packed column, respectively.

Because of the smaller sample size, the detection limit of the modified method was higher than Method 625 by a factor of five. Also, because of the acidic conditions used for the extraction, benzidine was not recovered. In all other respects the results were comparable to those obtained by Method 625. The method is therefore considered suitable for most solid wastes.

TOTAL CONTENT ANALYSIS METHODS

Metal Analyses

The total content digestion method used for metals in Task 6 was based on a method developed by the University of Washington and modified by Southern Research Institute. In this method an aliquot of the solid waste is placed in a clean glass ampule. Concentrated nitric acid is added to the ampule which is sealed and heated at 125°C for one hour. The digested sludge is filtered and analyzed by atomic absorption or ICAP.

The method requires a short digestion period, much shorter than most sludge digestion methods. Spike recoveries for all elements examined were quantitative. The sealed ampule permits a higher temperature to be used than would be acceptable with open beaker digestion, without loss of volatile metals. Once the samples are placed in the oven, it is not necessary to constantly monitor the progress to prevent the digestion from going to dryness. Since no HCl is used, the digestion is useful for silver. In fact, the single digestion is recommended for all elements; a considerable reduction in the time required for preparation over alternate methods requiring as many as four separate digestions.

A major problem encountered with the application of this method involves the transfer of the solid waste sample to the 25 ml ampule. The open end of the ampule is approximately one-fourth inch in diameter. For samples containing only small particles, the transfer is relatively simple. However, for solid wastes containing larger particles or for samples of a mud consistency, transfer is very difficult due to the restricted opening. Accurate weighing of the sample is also difficult, and the sample frequently sticks to the inner walls of the ampule neck. The sample must be removed from the neck of the ampule in order to allow proper sealing. Further, it becomes difficult to handle a potentially hazardous solid waste using recommended safety precautions such as rubber gloves. The sample is easily spilled on the balance and benchtop which must be carefully cleaned to prevent safety hazards.

Although no ampules exploded in the studies reported here, the possibility of a dangerous explosion must be considered when using concentrated nitric acid in a sealed ampule. A program initiated during the reporting of this leaching development study included the analysis of industrial waste using the sealed-ampule method for metals. An explosion occurred in the oven during the heating process which resulted in loss of all samples but did not involve personal injury or property damage. For re-analysis the ampules were individually placed in heavy containers made from pipe sealed at both ends. This safety precaution involves increased material costs and analysis time, however, the safety of the analyst and equipment is guaranteed. Appropriate safety precautions should be incorporated for this method.

Although quantitative spike recoveries were obtained for the elements analyzed in this study, further information is required to determine whether this method is universally applicable to all elements to be analyzed in solid wastes.

Volatile Organic Analysis

The CS_2 extraction method used for total content analysis involved dispersing the solid waste in water and treating it in the same manner as a leachate. This approach is the same as that used for the purge and trap method applied to total content analysis. The advantages and disadvantages of the CS_2 extraction method already discussed for leachate analysis also apply to total content analysis. Since much greater quantities of extractable components are often encountered in total content analyses, it may be necessary to temperature program the GC column to a higher temperature, e.g., 300°C, to ensure that most of the high-boiling components are eluted prior to the next run. The high temperature does not adversely affect the silicone capillary column used. However, this type of thermal cleaning of the GC column could not be achieved with the conventional packed column for volatile organics, 1 percent SP-1000 on Carbopak C, because of greater retentiveness and much lower temperature limitation.

The CS_2 extraction method worked very well for total content analysis and gave results that were comparable to those from the purge and trap method. The volatile components of concern appeared in the early portion of the chromatogram where there were fewer potential interferences.

Semivolatile Organics

The total content method for semivolatile organics involves homogenization of the sample in the presence of water with methylene chloride as the extracting solution. Base/neutrals are obtained by successive extractions under basic conditions and acids are obtained by successive extractions under acidic conditions. The two extracts are concentrated as separate fractions and cleaned up by gel permeation chromatography (GPC).

During the process of concentrating the extracts or while the concentrate stands at room temperature, insoluble material often precipitates. This precipitate can have two significant adverse effects. First of all it can interfere with the GPC cleanup. The precipitate settles out at the top of the column and causes an irreversible darkening and loss of column efficiency if manual column operation is used or it clogs up filters and valves if an automated operation is used. Secondly, it may serve as an adsorbent to remove some of the components of interest, especially the more polar components, and thus seriously affect the recovery efficiencies.

Recovery efficiencies also seem to be adversely affected by the presence of water during the extraction step. Recoveries for the more polar components, e. g., phenols and nitroaromatics, are often very poor and detection limits are abnormally high. The six homogenization-centrifugation-solvent removal steps in the method were found to be quite tedious and time-consuming.

Despite the above disadvantages of the method, the precision and accuracy of the method, as indicated by recoveries achieved with spiked samples, were generally adequate except for the more polar components.

FEASIBILITY OF IMPLEMENTATION

Leaching Method

The leaching method involves: (1) leaching a portion of the solid waste with an aqueous medium and (2) analysis of the aqueous medium for organic and metal components. In terms of apparatus and instrumentation, the analytical step requires: (1) extraction and concentration apparatus, (2) a packed column GC-MS system with associated data handling system and software package, (3) a purge and trap apparatus interfaced to the GC-MS system, and (4) a flame atomization atomic absorption spectrometer (AAS) or an inductively coupled argon plasma spectrometer (ICAP). For mercury, a special cold vapor purging apparatus interfaced to the AAS is required. The requirements for conducting the analytical phase are essentially identical to the wastewater priority pollutant methods, which are widely employed by a number of production-type analytical laboratories.

Because of the complex and diverse nature of leachates from solid wastes, cross contamination between sample extracts can be a problem. This problem was observed for the purge and trap method for determining volatile organics. For example, the use of this apparatus for analyzing still bottoms leachate caused severe carry-over into subsequent samples, due to the high quantity of volatile organics present. Since it is not possible to predict which leachates may create such problems, it is essential that the operator run frequent system blanks and examine the data from each sample for possible contaminants from the previous sample. The CS_2 extraction procedure for volatile organics, described in the experimental section, circumvents this problem since the same apparatus is not used for each sample.

The method for leachate generation requires the following apparatus and instrumentation:

- An agitation device, such as the NBS tumblers used in this study
- Bottles (2-liter capacity) with Teflon-lined caps to fit the agitation device
- A centrifuge, medium speed, capable of holding 200-ml glass bottles
- Centrifuge bottles
- Filter holder capable of being pressurized to 75 psi
- Various prefilters and membrane filters.

Except for the agitation device and filter apparatus, this equipment is readily available in analytical laboratories conducting organic analytical work. Both the NBS tumblers and filter apparatus can be readily purchased for a total cost of approximately $2500. Therefore, availability of instrumentation should not be a significant problem for laboratories wanting to implement the leaching method.

The highly diverse physical and chemical nature of solid wastes can be a problem in the leachate generation step, since a single set of procedures for filtration, and phase separation, may not be feasible for all types of wastes. The leachate generation method (using the NBS tumblers) described in the Experimental Section has been carefully devised to be applicable to as wide a range of solid waste types as possible. However, there are probably certain types of solid wastes which will cause some difficulty.

One specific example is an oily waste sample, which creates the problem of how to obtain a representative aliquot of the oily layers or film present at the surface of the leachate. When a thin layer or film is present, it is sometimes feasible to vigorously agitate the waste prior to withdrawing an aliquot for analysis, although questions always arise as to how much of the oil phase remained on the glass surface of the original container.

Problems can also arise from the presence of relatively large chunks (1 cm diameter or more) of debris in the sample, since this debris can cause the glass bottles to break during agitation. This problem can be circumvented by using polypropylene bottles, although contamination problems may arise for organic analysis.

A general problem in the area of solid waste analysis is how to obtain a representative sample or subsample of a solid waste. Current methods address this topic in only a general way, but specific sampling protocols for multiphase wastes, for example, need to be developed. This problem does affect the feasibility of implementing the leaching method, although accurate results cannot be obtained if a representative sample is not obtained.

Total Content Method

The apparatus and instrumentation required to conduct the total content method are identical to that required for the leaching method, except that the leachate generation apparatus is not required. The primary problem impacting on the feasibility of the method is the highly complex nature of the solid wastes. Certain organic compounds may be present at percent levels, thus overwhelming the smaller components in the chromatogram and contaminating the mass spectrometer. This problem can be severe in the purge and trap method for volatiles, as discussed previously for the leaching method.

COST TO IMPLEMENT

In calculating a cost to implement the leaching method several assumptions have been made:

(1) The analysis is to be conducted on a day to day basis. Therefore instrument installation and setup are not included in the cost estimate. However, instrument calibration has been included.

(2) A sample batch consists of a minimum of 10 waste samples and 2 quality control samples.

(3) A technician hourly rate (including all overhead and fee) is \$25 and a professional hourly rate is \$40. GC-MS instruments cost \$50/hour and AAS costs \$20/hour.

(4) AAS methods for metals will be used.

The costs for various steps in the procedure are listed in Table 45 on a per waste sample basis.

TABLE 45. ESTIMATED COSTS FOR ANALYZING TEN SAMPLES USING THE SOLID WASTE LEACHING PROCEDURE

	Materials	Professional Hours	Technician Hours	Instrument Cost	Total $
Leachate Generation	$20	0.2	4.0	10	138
Organic Analysis					
Volatiles	$20	1.5	2.0	100	230
Semivolatiles					
Extraction	$10	0.2	2.0		68
GC-MS	$5	2.0	2.0	120	255
Inorganic Analysis					
Sample Preparation	$10	0.2	1.0		43
Analysis	$5	0.2	4.0	40	153
Hg Sample Preparation	$15	0.2	0.4		33
Hg Analysis	$5	0.2	0.4	20	33
QA Review		1.5			60
Data Coordination		2.0			80
Project Supervision		1.5			60
	$90	9.7 hrs	15.8 hrs	$290	$1163

NOTES: The use of purge and trap rather than CS_2 extraction for volatiles will result in a cost increase of about $100/sample because lower sample throughput will be obtained.

Use of ICAP for metals other than Hg will reduce the cost by about $75/sample.

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APPENDIX

SOLID WASTE LEACHING PROCEDURE
(Battelle's Columbus Laboratories, November 1, 1980)

1. Scope and Application

1.1. This method describes a procedure for leaching waste materials with an aqueous medium to obtain a solution that can be analyzed to determine the components leached under the specified testing conditions.

1.2. This method is applicable to the preparation of a leachate that can be used to assess the potential mobility of chemical components from a solid waste placed in a landfill.

1.3. The particular aqueous leaching medium selected should reflect the most severe conditions expected at the specific landfill site of concern.

1.4. It should not be presumed that the method will give a leachate generated under controlled laboratory conditions that is the same as the actual leachate produced under variable conditions from a waste in the field.

2. Summary of Method

2.1. A 75-g sample of the waste is mixed with 1500 ml of a selected aqueous medium in a closed container and leached by tumbling the mixture in an end over end fashion for 20 hours.

2.2. The mixture is centrifuged and filtered to give an aqueous solution that can be analyzed to determine the components that were leached from the waste.

3. Interferences

3.1. Small amounts of water-immiscible oils or organic solvents present in the waste that might contribute significantly to the potential mobility of certain hazardous components may be removed during the centrifugation and filtration steps. The final leachate in such a case cannot be used to assess the total potential mobility of hazardous components in the waste. Large amounts of water-immiscible oils or organic solvents present in the waste may become part of the final leachate and make it difficult or impossible to obtain representative aliquots of the leachate for analyses. These constituents may also destroy the cellulose ester membrane filter used in the filtration step. Any water-immiscible liquid phase present in a waste should be separated out prior to leaching and analyzed separately for total content to determine possible influence on the potential mobility of hazardous components.

3.2. Sample containers, centrifuge bottles, filtration assembly, reagents, and distilled water used must be demonstrated to be free from interferences that might be present in leachates at the minimum levels of interest.

3.3. Significant amounts of highly volatile organic constituents, e.g. vinyl chloride or methylene chloride, may be inadvertently lost from the leachate during sample transfers. However, because varying amounts of such components will undoubtedly be lost during landfilling and sampling, the method is not intended to retain them completely.

4. Apparatus and Materials

4.1. Tumbler: a device that is capable of holding one or more tumbler bottles and turning them end over end approximately 30 times per minute, such as the four-place tumbler designed by National Bureau of Standards which is available from Associated Design and Manufacturing Company, Alexandria, Virginia.

4.2. Tumbler bottle: 1800- to 2500-ml wide-mouth screw-cap bottle (e.g. Wheaton No. 348522 roller culture vessel). Caps must be lined with Teflon.

4.3. Centrifuge: capable of holding four or more 200-ml centrifuge bottles and operating at 2000 rpm (e.g. IEC No. 7165).

4.4. Centrifuge bottles: 200-ml screw-cap bottles (e.g. Corning No. 1261). Cap must be lined with Teflon.

4.5. Filter holder: 142mm diameter with 1.5 liter reservoir capable of being pressurized to 75 psi (e.g. Millipore No YT30142HW).

4.6. Glass fiber prefilter pads: fine 124-mm (e.g. Millipore No. AP15-124) and coarse 124-mm (e.g. Millipore No. AP25-124).

4.7. Nitrocellulose membrane filter: 142-mm (e.g. Millipore No. HAWP-142).

4.8. Sample vial: 40-ml capacity with screw-cap (e.g. Pierce No. 13075).

4.9. Sample vial septum: Teflon-faced silicone (e.g. Pierce No. 12722).

4.10 Syringe: 50-ml glass hypodermic syringe with Luer-Lok tip.

4.11 Wide-bore syringe needle: 20-cm 16-guage stainless steel needle (e.g. Bolat No. BB829).

4.12 Glass sample bottles: 500-ml or 1-liter narrow-mouth bottles with Teflon-lined screw caps.

4.13 Polypropylene sample bottles: 500-ml or 1-liter screw-cap bottles.

5. Reagents

5.1. Leaching media: one or more of the following solutions may be used.

5.1.1. Distilled water: water that is demonstrated to be free of organic and inorganic interferences at the minimum levels of interest in the subsequent leachate analyses that will be performed.

5.1.2. Acetate buffer: 0.1 M, pH 4.0; 8.2 g of sodium acetate trihydrate (ACS) and 5.7 ml of glacial acetic acid (ACS) per liter in distilled water.

5.1.3. Citrate buffer: 0.05 M, pH 5.0; 10.5 g of citric acid monohydrate (ACS) and 4.0 g of sodium hydroxide (ACS) per liter in distilled water.

5.1.4. Citrate buffer containing 0.01 percent Igepal CO-630: 0.05 M, pH 5.0; 10.5 g of citric acid monohydrate (ACS), 4.0 g of sodium hydroxide (ACS), and 0.1 g Igepal CO-630 per liter in distilled water. Igepal CO-630 is a nonionic detergent produced by GAF Corporation.

5.2. Nitric acid (1 + 1) (ACS)

6. Sample Collection, Preservation, and Handling

6.1. A representative sample of the waste to be tested should be obtained by using an ASTM standard method that can be applied satisfactorily (e.g. D140-70, D346-75, D420-69, D1452-65, or D2234-76) or by using methods described in "Samples and Sampling Procedures for Hazardous Waste Streams" EPA 600/2-80-018, January 1980. It is particularly important that the sample be representative with respect to surface area and solids contents which directly affect the leaching characteristics.

6.2. A minimum sample of 5000 g should be collected and sent to the laboratory in a closed container that will not be attacked by the waste material. In most cases a polypropylene container will be suitable.

6.3. Samples which have not been biologically or chemically stabilized, i.e. those that might undergo significant biological or chemical change at room temperature, should be maintained at 0-5°C, including shipping, and leached within 48 hours. Stabilized samples may be shipped and stored at room temperature.

7. Leachate Generation

7.1. Crush or cut the sample as necessary to reduce the particle size to approximately 1 cm. Avoid excessive particle size reduction.

7.2. Take a 75-g representative sample of the waste to be tested and place it in an extraction bottle with 1500 ml of leaching medium. Tighten the cap on the bottle and tumble the mixture at 20-40°C for 20 ± 2 hours.

7.3. Transfer as much of the mixture as required for subsequent analyses to 200-ml glass centrifuge bottles. Shake the mixture immediately prior to filling the centrifuge bottles if necessary to obtain representative samplings of any oil-water dispersions. Centrifuge at approximately 1500 RCF for 30 minutes at 20-30°C. (Note: This centrifugation step can be deleted if the subsequent filtration step can be performed without excessive clogging of the filters. In most cases the mixture can simply be allowed to stand for 30 minutes and the supernatant used for volatiles analysis and for the filtration step.)

7.4. Obtain a sample for volatiles analysis by completely filling a 40-ml vial with the supernatant from one of the centrifuge bottles from 7.3. Fill the sample vial in such a manner that no air bubbles pass through the sample as the vial is being filled. If the centrifuged sample contains any oil, organic solvent, or particulate material floating on top of the water, use a syringe with a wide bore needle to withdraw the sample from the water layer below such material. Do not attempt to analyze the oil or organic solvent layer. Seal the vial with a Teflon-faced septum and screw-cap and store it at 0-5°C in an inverted position until the time of analysis.

7.5. Process the remaining supernatant from 7.3 for metals and semivolatiles analysis. If a discrete oil or organic solvent layer is present transfer the layer to a tared bottle using a disposable pipette, determine the weight, and analyze it separately if necessary.

7.6. Decant the aqueous supernatant and filter it through one of each type of glass fiber prefilters and a 0.45 μ membrane filter. Determine the weight or volume of the filtrate. Use the filtrate for semivolatiles analyses and metals analyses. Store the portion of the filtrate that is to be used for semivolatiles analyses in glass bottles with Teflon-lined screw-caps at 0-5°C until time of analysis. To the portion of the filtrate that is to be used for metals analyses add (1 + 1) HNO_3 to lower the pH to <2 and store at room temperature in screw-cap polypropylene bottles.

8. Quality Control

8.1. Before leaching any waste samples, demonstrate through the complete processing of a method blank that no analytical interferences will result.

8.2. Process one method blank for every set or every ten samples analyzed.

8.3. For every ten samples of a single type of waste, process at least one sample in triplicate.